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ZONE REFFINING
By PARR (NL)

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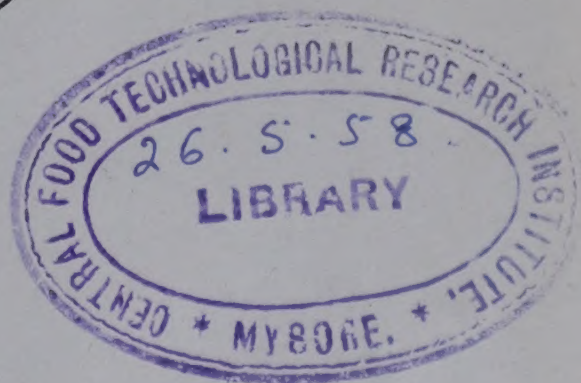
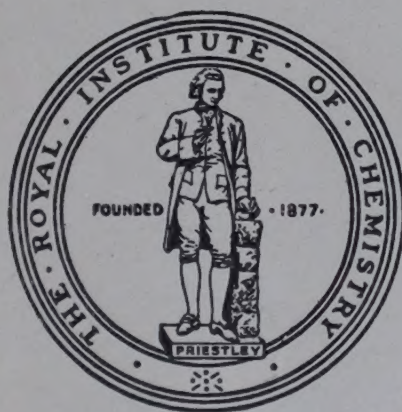
ZONE REFINING

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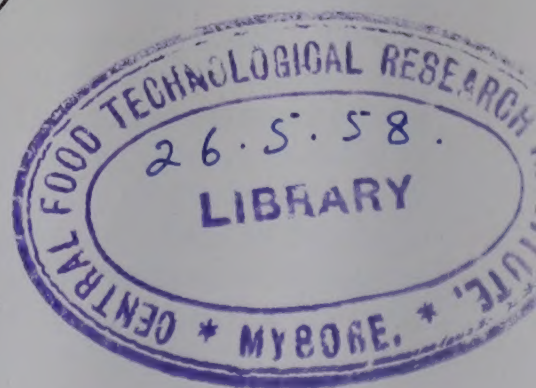
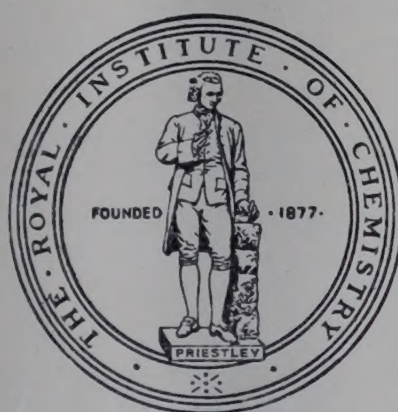
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of the Institute on 13 March, 1957, at the Iron and Steel
Institute—Dr C. C. Hall in the Chair.*

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ZONE REFINING

By N. L. PARR, A.M.I.MECH.E., A.I.M.

The need for improved methods of purification has grown out of the demand of those engaged in various new technological developments for a more intimate knowledge of certain elements in their highest state of purity. One such method of purification, which has sprung into prominence during the last five years, largely as a result of the efforts of workers in the field of semi-conductors, has been termed 'zone refining'. As the title suggests, the process is in some ways similar to fractional crystallisation, as it involves the removal of impurities by a solidifying front. The method is applicable to any crystalline substance that exhibits a difference in soluble impurity concentration in the liquid and solid states at the point of solidification.

The phenomenon is a segregation process similar to that studied and provided for in the foundry for many years, but credit for the application of the factors involved to a purification technique goes to workers with transistors and diodes who were searching for methods of obtaining small and critical concentrations of impurities in single crystals. As a result of their success, the methods they have employed have been the subjects of many technical papers since 1952, of which the contributions by W. G. Pfann^{1,2} of the Bell Telephone Laboratories Inc. have been amongst the most noteworthy. Accordingly, the method has already been employed for the purification of a number of organic and inorganic substances, particularly metals.

Rapid advancement of the method has been aided by the many new laboratory techniques available to the research worker, which include improved high vacuum equipment, super-pure atmospheres and high-frequency and dielectric heating. However, the assessment of the degree of success achieved comes within the province of the analytical chemist who must now consider the estimation of impurities present to the extent of only 10^{-3} to 10^{-9} p.p.m.

Metallurgists, perhaps, are making the widest use of zone refining, in order to study the profound effects of sometimes minute quantities of impurities on the physical and chemical properties of metals. Besides producing metals of extreme purity in order to study deformation and fracture processes, the need for methods of separating elements with long half-lives is increasing in the field of nuclear energy. The zone-refining technique can also be modified to produce a variety of physical states in single or polycrystalline form hitherto unobtainable. One of the more recent applications of the technique has been in the purification of organic compounds, whilst, at the other end of the temperature scale, zone refining is being employed for the purification of refractory oxides and related compounds.

As an introduction to the process it is convenient to study the type of segregation commonly experienced in certain alloys, for which special provision is made in the foundry by employing refractory feeder heads in the manner illustrated in Fig. 1. Although these feeder heads are

provided mainly in order to accommodate shrinkage, they also serve to provide an expendable head, which is found to be rich in slag and soluble impurity. While accumulation of the slag results largely from a flotation process, the soluble impurities are moved by a segregation phenomenon associated with progressive solidification.

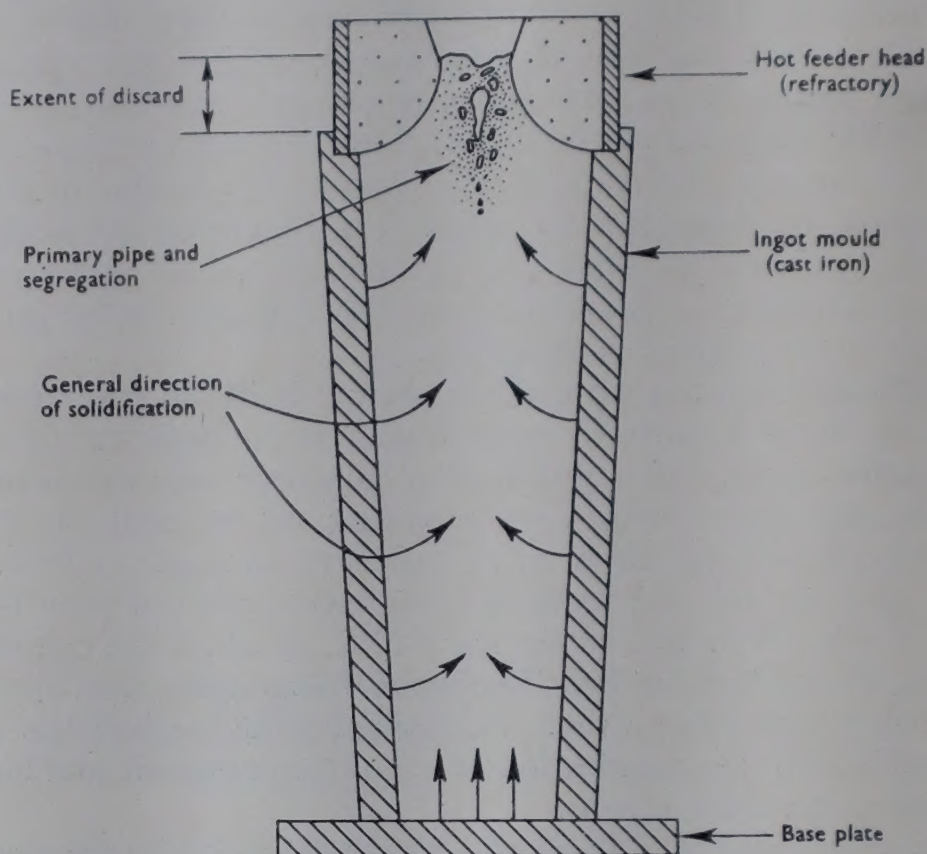


FIG. 1. Design of Ingot Mould for concentrating segregates and piping in the head of an ingot

With such alloys the segregation is usually visible under the microscope as 'coring', which often takes the form illustrated in Plate I. This arises from the fact that successively deposited layers of solidified metal upon the original dendrite exhibit a gradual compositional change, which is readily discernible on polished and etched surfaces. It is explained by the differences in the liquid and solid solubilities of one element in the other over the whole range of solidification, which occur as a result of the sluggishness of solid state diffusion. This characteristic of solidification is exploited for zone refining and, although the example given is concerned with fairly large amounts of one element in the other, the same process occurs where only minor proportions of solute impurity in an almost pure solvent are involved.

The general term for this technique is *Zone Melting*, which, as the title suggests, broadly embraces the application of such segregation characteristics by the control of the rate and direction of solidification. As we shall see later, this is usually achieved by slowly traversing a comparatively long solid charge with a narrow molten zone, but several modifications to this technique, such as *Directional Solidification* and *Zone Levelling*, have been employed, the last-mentioned to achieve complete homogenisation of the impurity.

The degree of success that can be achieved is a function of the magnitude of the difference between the solid and liquid solubilities of one element in another at the point of solidification, which can be calculated from knowledge of the phase equilibria and is known as the *Segregation Coefficient*. Where the method is applied primarily for purification purposes the process is termed *Zone Refining*.

These processes will be considered individually, but before describing them in detail mention must be made of other factors affecting the degree of purification during zone refining and allied processes. These include the liberation of elements of higher vapour pressure than their parent by out-gassing, volatilisation or sublimation and the possible removal of insoluble impurities of different density by flotation or gravitation. Although these are secondary to true segregation, they frequently play an important role during the practical application of the method by providing means for the removal of many impurity elements detrimental to the true zone-refining process.

EQUILIBRIA DURING SOLIDIFICATION; SEGREGATION COEFFICIENT

In order to illustrate the difference of solute solubility in the liquid and solid phases during solidification it is convenient to examine a phase equilibrium diagram for a simple solid-solution binary alloy such as is illustrated in Fig. 2.

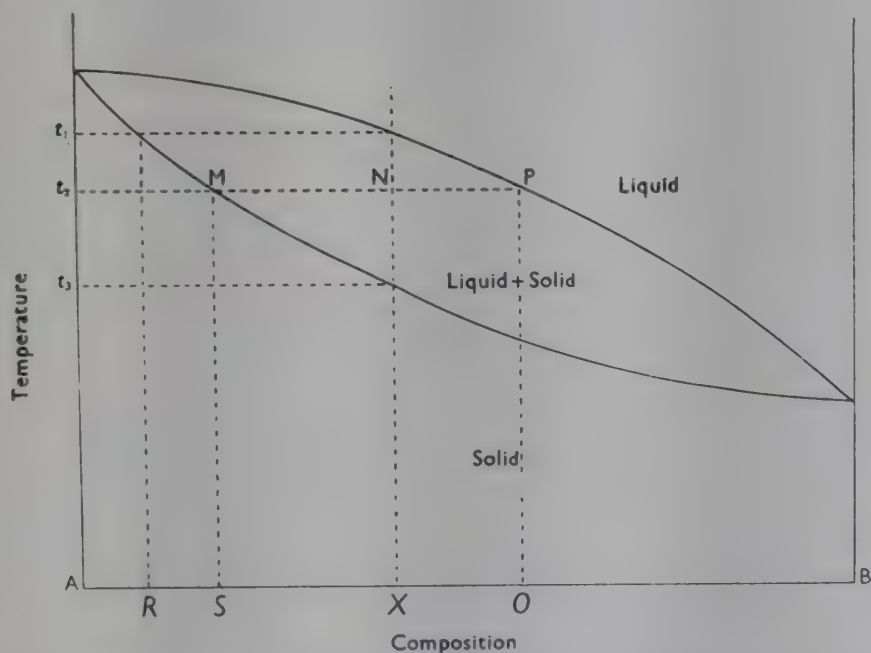


FIG. 2. Phase diagram of two metals completely soluble in the liquid and solid states

According to the phase diagram, an alloy of composition X should, upon solidification, be a single phase substance of uniform composition. Owing, however, to the slowness of solid-state diffusion, equilibrium is not maintained during solidification, and the result is the cored or segregated crystal structure illustrated in Plate I. This results from the fact that the first material to be deposited upon cooling to temperature t_1 , of

composition R , is in equilibrium with the remaining liquid at this temperature. As the temperature continues to fall and the composition of the solid tends to approach that of its theoretical X , adjustment of the composition of the material previously deposited to its theoretical value should normally take place by absorption of the remaining liquid and by solid-state diffusion. At an intermediate temperature t_2 there should be NP parts of solid of composition S in contact with NM parts of liquid of composition O . Finally, at t_3 the metal is entirely solid and should consist of homogeneous crystals of a solid solution of composition X . Such compositional adjustment during cooling is not completely achieved in practice with normal rates of cooling, owing to the slowness of solid-state diffusion, and the result is the metallographical structure already identified as 'coring' (see Plate I). The greater the difference between the liquidus and solidus lines for a given composition the greater will be the chance of coring. The ratio of the solid and liquid solubilities of one element in the other may be expressed as the *Partition* or *Segregation Coefficient*. It is this coefficient that governs the chances of separating successfully one element from the other by the zone-refining technique.

As the technique is used chiefly with almost pure elements, only the extreme ends of such phase diagrams should be considered, where the solidus and liquidus lines are represented as their tangents at their point of intersection, as given in Fig. 3.

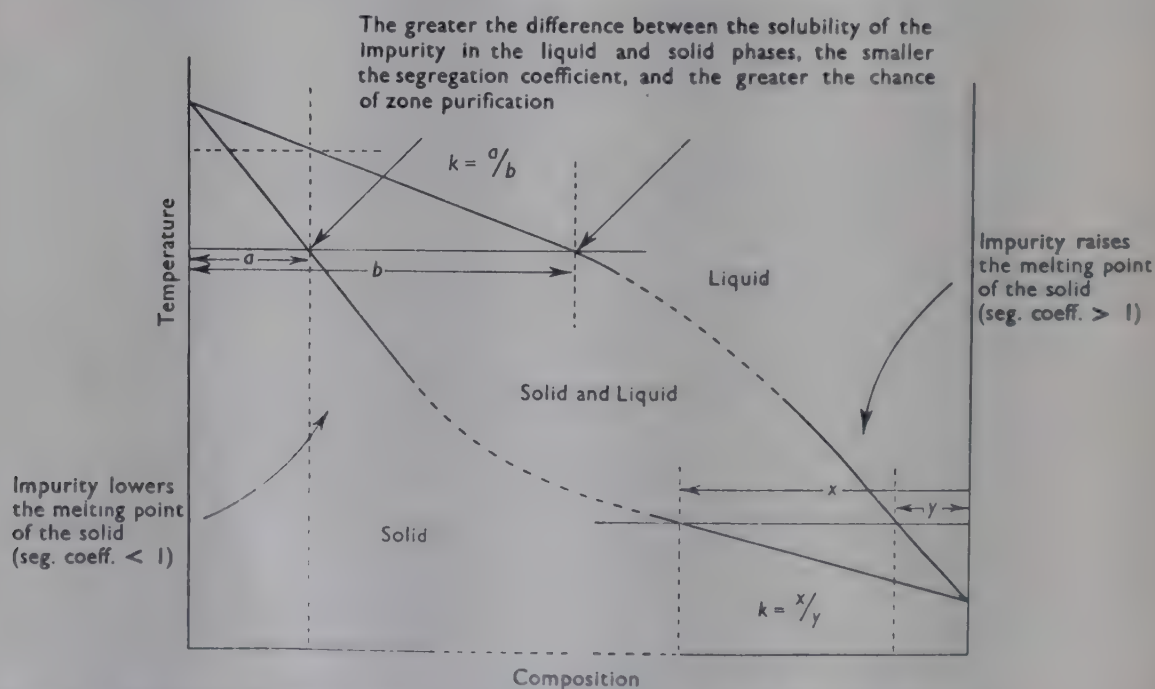


FIG. 3. Portions of the Phase Diagram, shown in Fig. 2, for an almost pure material where the liquidus and solidus lines can be considered linear, thus allowing the ratio of the solubility of impurity in the solid to that in the liquid to be expressed as the segregation coefficient, k

The segregation coefficient k may therefore be expressed as the ratio of the relative slopes of the solidus and liquidus lines. Provided that an accurate equilibrium diagram is available, the segregation coefficient for a binary system can be calculated simply from the ratio of the intercepts of the solidus and liquidus tangents with any horizontal line drawn from

the temperature axis. The closer the liquidus and solidus lines, the nearer will the segregation coefficient approach unity, thereby rendering the zone-purification process impracticable.

Impurities which cause the melting point of the parent metal to be lowered will concentrate in the remaining molten metal, and those causing it to be raised will tend to accumulate in the solid.

k Segregation coefficient

C_0 Initial concentration of solute in the liquid

C_s Concentration of solute in solid immediately adjacent to the solid/liquid interface kC_L

C_L Concentration of solute in remaining liquid

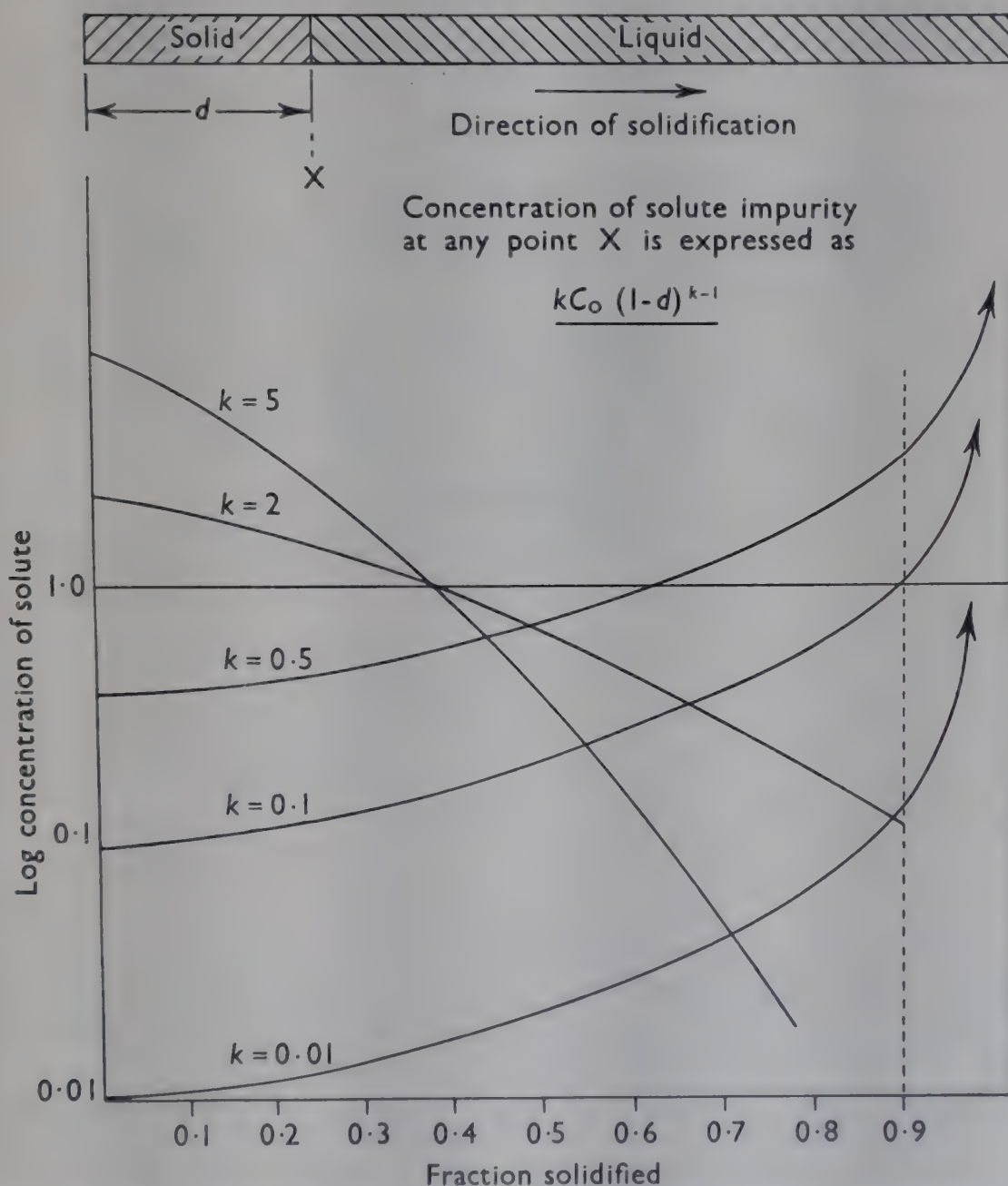


FIG. 4. Distribution of solute impurity, for various values of segregation coefficients, with directional solidification

From these remarks it can be seen that the true zone-refining technique can only be applied where the material concerned, which might be an element or a stable compound, possesses favourable segregation coefficients in respect of its impurities.

Purification may be achieved either by directional solidification or by causing a narrow molten band to traverse a comparatively long solid bar (zone refining). Alternatively, and for special cases, a solidified band can be passed along a tube or column of liquid.

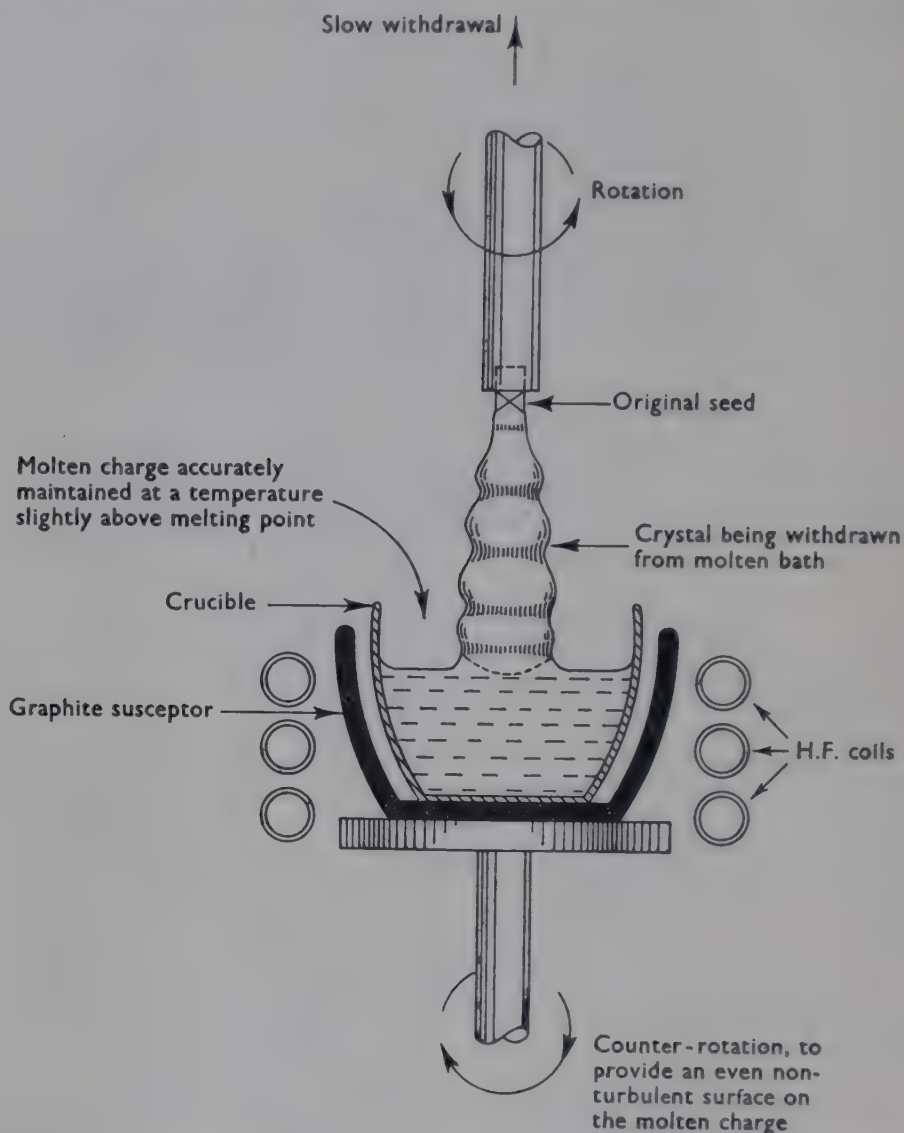


FIG. 5. Kyropoulos technique for withdrawing a crystal in solid bar form from a molten bath

DIRECTIONAL SOLIDIFICATION

In theory, when molten material is permitted to solidify unidirectionally at a rate sufficiently slow to permit solid-state diffusion, a homogeneous product should be obtained, and the process could then be termed *Equilibrium Freezing*. This ideal condition is not achieved in practice, however, owing to the extreme slowness of solid-state diffusion, but by controlling the rate of directional solidification it is possible to achieve a degree of directional purification. Furthermore, as solid-state diffusion may be considered negligible for all practical purposes, a good idea of the degree of purification likely to be achieved can be obtained

if the segregation coefficients of the elements in question are known. For such estimations it is assumed that diffusion is zero in the solid state and complete in the liquid phase, particularly when the process is aided by stirring.

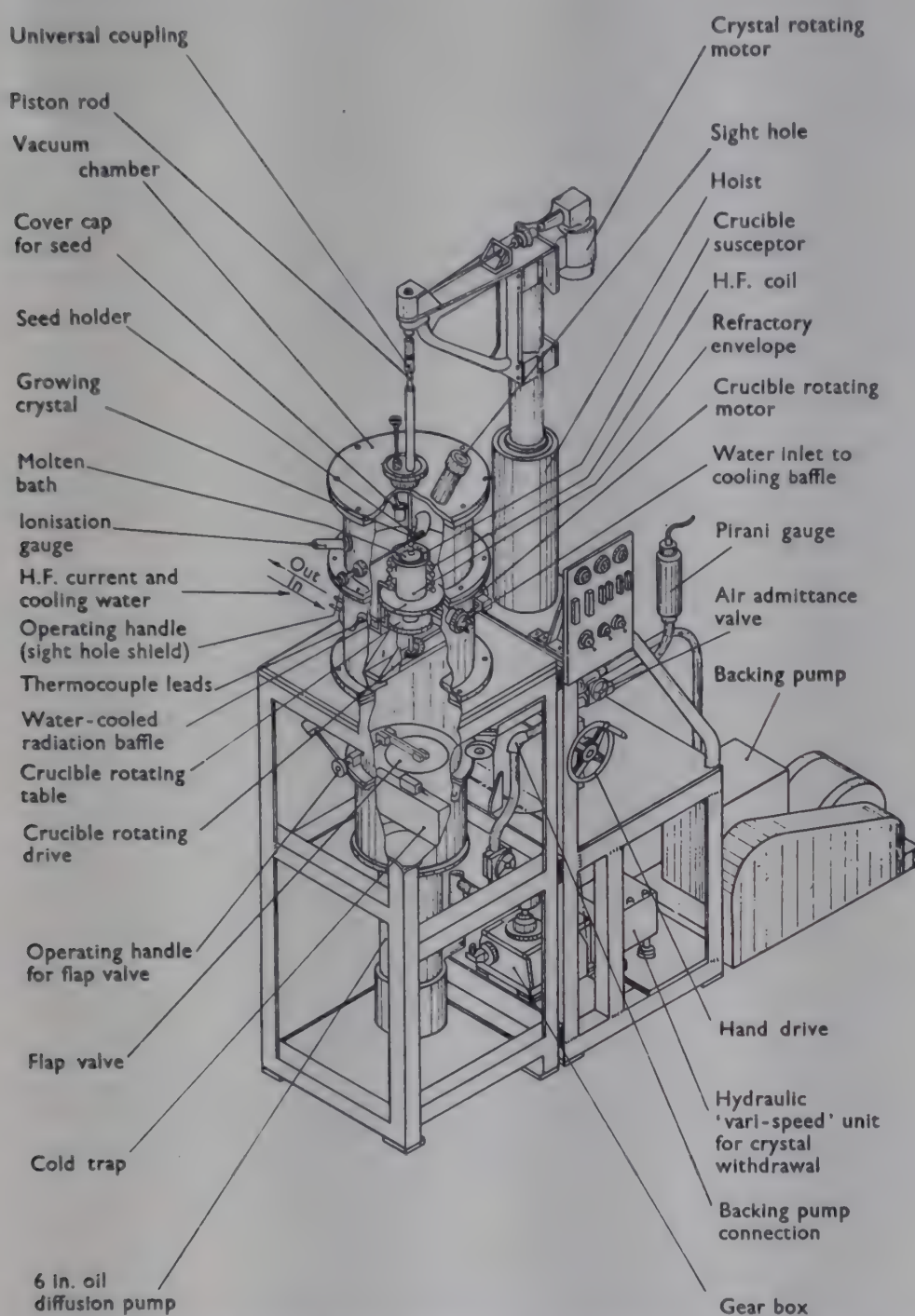


FIG. 6. Equipment for growing single crystals of metals by the Kyropoulos technique

Provided the segregation coefficient for a particular solution and solute is known, the distribution of impurity along a directionally solidified bar can be expressed in terms of the initial concentration and fraction of the length solidified as $kC_0(1-d)^{k-1}$, as illustrated for a range of segregation coefficients in Fig. 4.

Directional solidification is not very attractive as a purification process, as the last areas to solidify (in the case of k values less than unity) would contain a comparatively high concentration of impurity which would

have to be discarded before the charge was remelted to effect further directional purification cycles. This would be wasteful and would introduce the possibility of recontamination from the crucible or atmosphere with each successive remelt. A modification of this method is employed for the production of single crystals by the well-known Kyropoulos technique, in which a growing crystal is slowly withdrawn from a bath of molten material, as shown in Fig. 5 and Plates II and III.

This technique involves the introduction of a seed to the surface of a bath of molten material, and by exercising extremely careful manipulative and temperature control it is possible slowly to withdraw a bar of material, the tail of which will contain correspondingly higher proportions of impurity. The method is fraught with great practical difficulty and, as a purification process, suffers (as with directional solidification) by loss of valuable material as a result of the inevitable discard, and also from the almost inevitable recontamination attendant upon remelting. The method is used mainly for the production of single crystals (often on zone-refined materials). Typical equipment designed at the Admiralty Materials Laboratory to produce single crystals of silicon in this way is shown in Fig. 6.

Each of these methods of directional solidification is essentially a one-pass operation and is thus wasteful and inefficient. Furthermore, the solidified mass will have an impurity gradient from one end to the other, unless it is remelted, and even this does not guarantee complete homogenisation. The Kyropoulos technique is, however, much used for the production of single crystals from already purified material.

The difficulties experienced with directional solidification are overcome if a molten zone is made to traverse a comparatively long solid bar of the material to be purified, or conversely, a solid zone is made to traverse a length of liquid. Such a method would lend itself to repeated purification passes without the need to disturb the mass being purified. It can also be used to produce a deliberate impurity gradient, to homogenise a product or to establish a variety of solid-state conditions.

The practical difficulties and limited application of the solid-zone technique restrict its use to materials with melting points close to or below ambient temperature, but as the factors concerned are the same as for molten zone refining, this will now be described in detail.

MOLTEN ZONE REFINING

When a molten zone is caused to traverse a solid bar it has both solidifying and melting liquid/metal interfaces. At the melting interface, new material is continually being introduced into the molten pool, thereby keeping up a constant supply of impurity. Where this impurity lowers the melting point of the solvent the freezing-to-liquid interface is constantly releasing atoms of impurity, which then accumulate in the molten zone and are moved towards the tail of the bar, *i.e.* in the same direction as zone movement. Where the melting point of the solvent is raised, deposition of atoms of the impurity element is favoured by the solidifying phase, which thereby tends to give progressive purification in the

direction of zone movement. The efficiency of the process will depend upon the width of the zone and its speed of travel, as clearly, if the zone movement is extremely slow, equilibrium may be obtained by solid-state diffusion, whereas too great a speed of travel may result in the re-deposition of impurity atoms before they can diffuse away into the molten pool.

Assuming that the width of the molten zone and its speed of travel are at an optimum, the redistribution of the impurity caused by traversing a bar of material with a molten zone, in terms of various segregation coefficients, can be seen in Fig. 7.

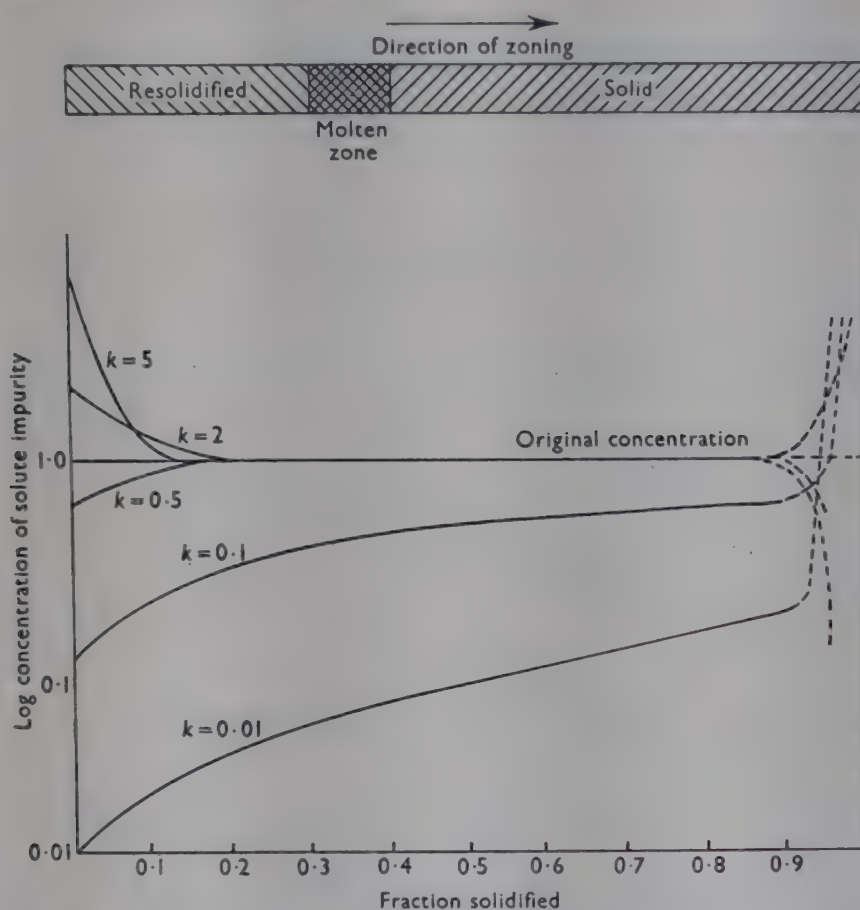


FIG. 7. Concentration and distribution of impurity along a bar traversed by a molten zone, for materials with various segregation coefficients

With a solvent whose segregation coefficient in relation to its solute approaches unity, *e.g.* $k = 0.5$, the material first deposited behind the moving zone will be purer, but as the zone advances and continues to take up more impurity, so that equilibrium conditions are less favourable than they were, the solidified face will become correspondingly less pure. When a state is reached such that the composition of the material being deposited is equal to that of the material being taken up by the melting face, a steady state is reached, and no compositional change occurs until the zone reaches the end of its travel, where it solidifies by directional solidification to give a rapid increase in impurity content. The plateau is reached at several times the zone length for systems with segregation coefficients of 0.5 and sooner with higher coefficients, until the process is rendered inoperable.

Impurities that tend to raise the melting point of the solvent and which have segregation coefficients greater than unity are subject to a reversed but much less efficient process, the moving liquid zone becoming progressively purer.

Materials with lower segregation coefficients (k values of 0.1 and 0.01) will respond to zone purification treatment in the manner indicated in Fig. 7. In such cases the original concentration of impurity will not be reached in the redeposited metal in a practical length of bar except in the

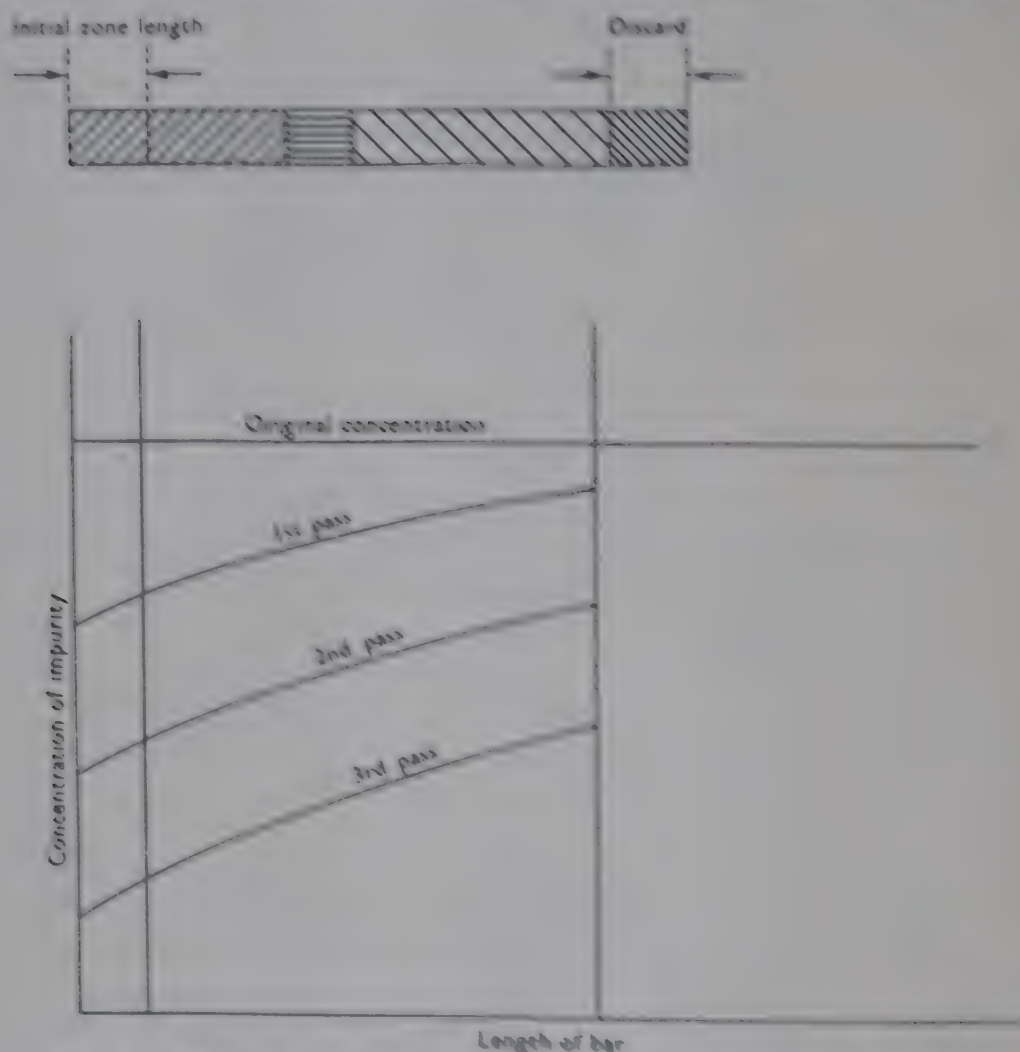


FIG. 8. Effect of repeated passes of a molten zone on distribution and concentration of impurities

very last sections to solidify. If the process is repeated with a second and third pass of the molten zone without disturbing the bar, the distribution of impurity in terms of concentration against length zoned takes the form given in Fig. 8.

There will be a gradual decline in efficiency of zone purification with each repeated pass to a point where the limit of solute distribution may be reached. This is a function of the segregation coefficient, and final distribution may not be achieved until many passes have been made and the concentration of impurity has been reduced to a very low level (as in a nickel/copper system). After the final pass, there may be a considerable impurity gradient along the bar, which rises in a very steep manner at the end corresponding to the direction of zoning. This end must be

discarded and the purified portion homogenised by remelting. Alternatively, uniformity in the distribution of the remaining impurity can be achieved *in situ* by giving the bar a number of zone passes in alternate directions, making sure that the end zone containing the high impurity content is excluded. The effect of this procedure on the distribution of impurity can be seen in Fig. 9, and the final useful length represents the major proportion of the original bar.

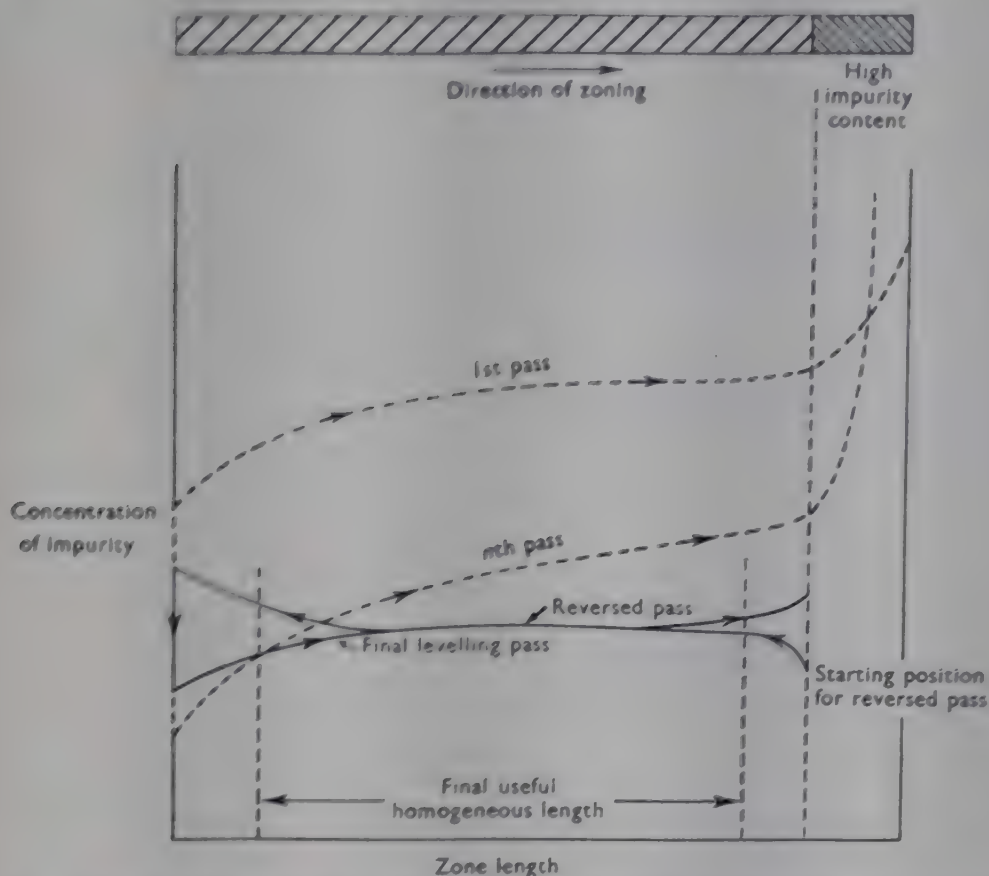


FIG. 9. Zone levelling process, consisting of a number of reversed cycles (omitting area of high impurity content)

Zone purification, coupled with zone levelling or allied techniques, may be used to produce wide variations of solute concentration in a bar of solvent. Solute elements can be introduced deliberately or dispersed or segregated to give desired impurity values or gradients. The method can also be used for controlling the number, size and shape of crystals in the bar aggregate.

The principles of the zone-purification process apply, not only to simple solid solubility systems, but also where eutectic or peritectic reactions produce compounds in equilibrium with other compounds, solid solutions or elements with the desired differences in solid and liquid solubility to give favourable segregation coefficients. This aspect has been covered in detail by Goodman.³

Generally speaking, all impurities that lower the melting point of their solvents segregate in the direction of solidification or zone movement and, conversely, those that raise the melting point tend by a less efficient procedure to segregate in the opposite direction to that leading to solidification. Provided they have favourable segregation coefficients, a

number of impurity elements may be removed simultaneously by the moving molten zone, and the relative rates of purification will differ according to the segregation coefficients involved.

THE INFLUENCE OF ZONE WIDTH AND ZONE SPEED

So far, diffusion has been considered to be negligible in the solid phase and complete in the molten zone. However, this is not completely so, particularly in the molten zone near the freezing face, where rejected solute atoms have to be transported away into the molten zone

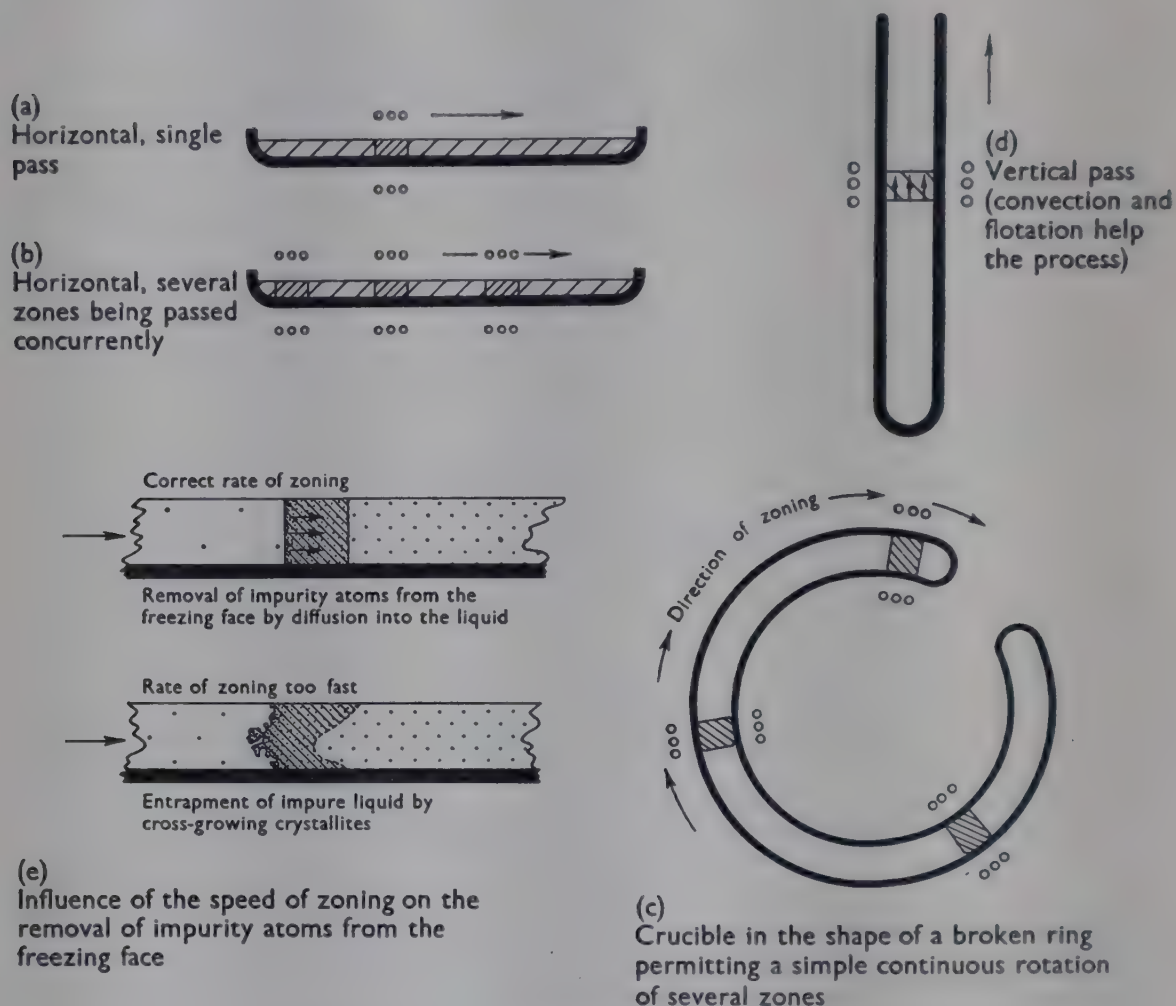


FIG. 10. Simple forms of zone purification

either by diffusion, convection or by mechanical stirring. Thus, the rate of solidification must be much more rapid than the rate of solid diffusion and yet not too fast to prevent reasonably efficient diffusion of the impurity into the molten zone. Any mechanical aid to liquid diffusion will increase the efficiency of the process, by mixing and by permitting zone refining to be carried out in the comparatively rare cases where the rates of solid and liquid diffusion of the particular elements concerned are close.

Another factor which may influence the speed of zoning is the possibility of irregular crystallisation at the solidifying face, such as is shown in Fig. 10. This may occur when the speed of zoning is too fast, and liquid containing a higher proportion of solute atoms is entrapped

by cross-growth before it can diffuse into the main body of the molten zone. The effect may be particularly evident where the liquid phase is viscous.

Speed of zoning is also influenced by practical considerations, and the precise speed to be adopted in order to achieve maximum efficiency is a balance between these and theoretical considerations, which have been studied by Burton *et al.*⁴ Speeds of between $\frac{1}{4}$ in. and 6 in. per hour have been successfully employed for metals. A stable and compact zone is essential to success and will depend upon the heat input required, which in turn depends upon the melting point, specific heat, latent heat of fusion, emissivity and the thermal conductivity of the solvent. It is thus simpler to produce a narrow molten zone in a material of high melting point and poor thermal conductivity than in a material whose melting point is near to ambient temperature and which is a good conductor. The speed of zoning will also influence the size and directionality of the crystals forming the aggregate. Under very closely controlled conditions and by nucleating solidification from a single crystal, it is possible to convert a polycrystalline aggregate into a single crystal during zoning with perhaps even greater chances of purification due to the single growing front. The influence of the length of the molten zone, in relation to the length of bar to be traversed in terms of impurity distribution, has already been discussed and illustrated in Figs 7, 8 and 9.

ZONE REFINING IN PRACTICE

The possibility of applying the zone refining technique to a particular material has been shown to be dependent upon the segregation coefficient of the solvent and solute, the physical properties of the material in relation to equipment available and the ultimate chemical and physical properties desired in the zoned bar.

HORIZONTAL METHOD

The simplest arrangement is that shown in Fig. 10(a), where the substance to be purified is supported horizontally in a boat or crucible and the molten zone is arranged to pass along the charge, either by moving the crucible through a hot zone or by causing a hot zone to surround and pass over the charge. Economy in time can be effected if several molten zones can be traversed simultaneously at spaced intervals, as illustrated in Fig. 10(b). This, however, is only possible where the charge is a poor conductor of heat, owing to the possible spread of the molten zones (which occurs in materials of high conductivity), unless the bar being purified is exceptionally long or alternate heating and cooling coils are employed. Continuous unidirectional movement of the hot zones can be achieved if the bar is held in a crucible or container in the form of a broken ring, as shown in Fig. 10(c). The methods described are typical of the more commonly used batch processes, but the development of a continuous zone-refining process, by employing the counter-current movement of voids and the purified and impure material in two separate arms of an inverted U-tube containing a common feed, is at present being undertaken.²

VERTICAL METHOD

Vertical support of the charge is adopted for some materials, particularly where flotation or gravitation can assist the removal of impurity elements and compounds differing in density from the solvent. This effect is particularly helpful for the removal of fairly large inclusions and self-slagging impurities. Vertical travel of the zone is also conducive to the transport of impurity atoms away from the solidifying face by convection.

MASS MOVEMENT

Differences in the specific volume of a substance in its solid and liquid states can give rise to difficulties, such as the cracking of completely filled and closed containers. Where the horizontal method is employed there

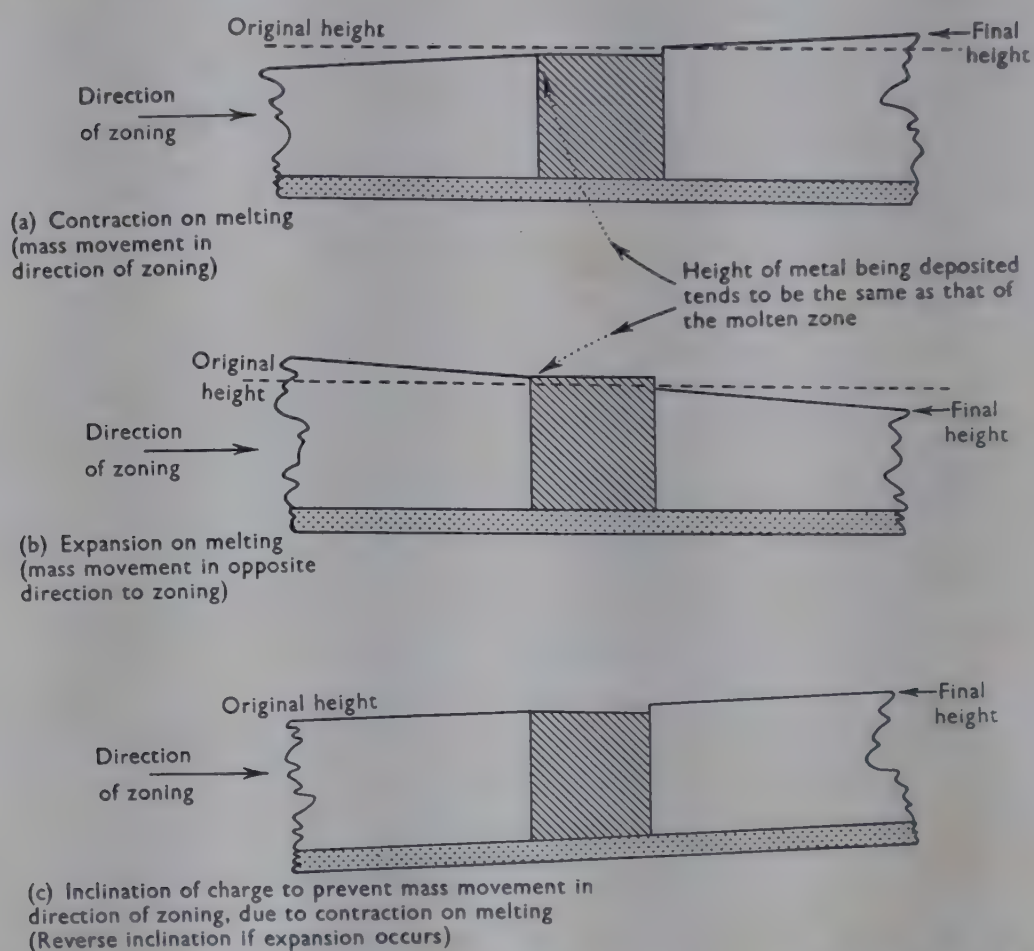


FIG. 11. Method for overcoming a gradual mass movement during zoning due to changes in specific volume during melting (the diagrams give exaggerated levels after several passes in one direction)

will be a gradual transport of matter towards one end or other of the bar, depending upon whether there is a contraction or expansion upon melting. This is illustrated diagrammatically in Fig. 11.

Although the effect may only be slight for each pass, it can reach undesirably large proportions where multi-passes are being employed and may also alter the delicate thermal balance governing the zone width. The simplest way of overcoming this difficulty is to incline the charge at a correct angle in order to balance out the effect.

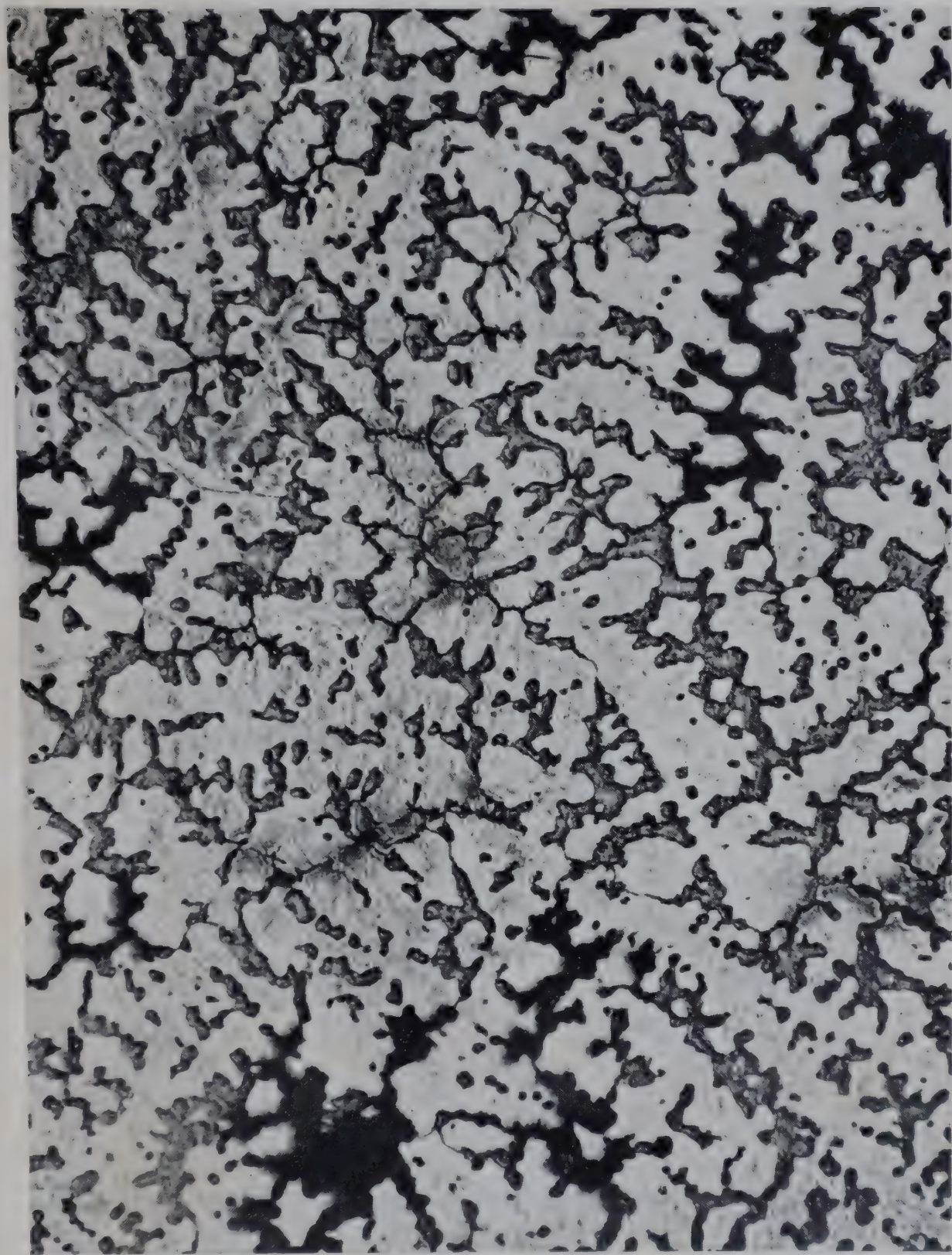


PLATE I. Coring in a Nickel-Copper Alloy

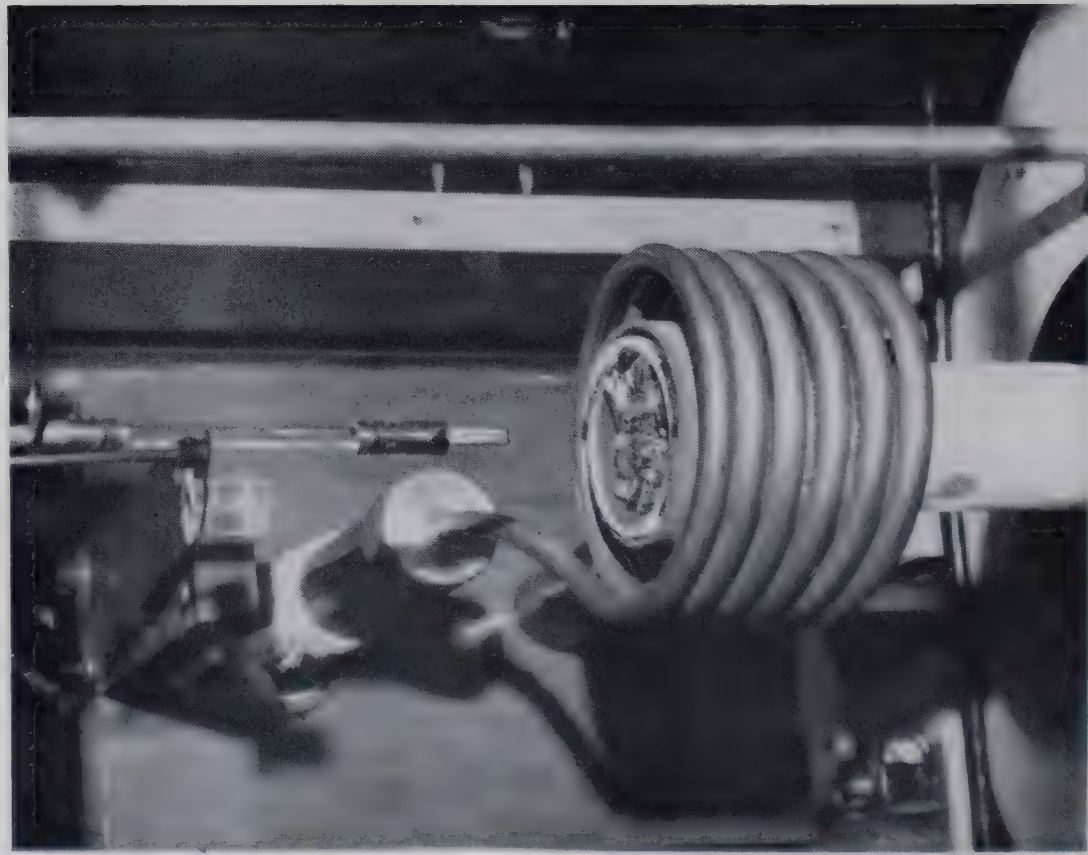


PLATE II. Apparatus for growing a single crystal by the Kyropoulos technique

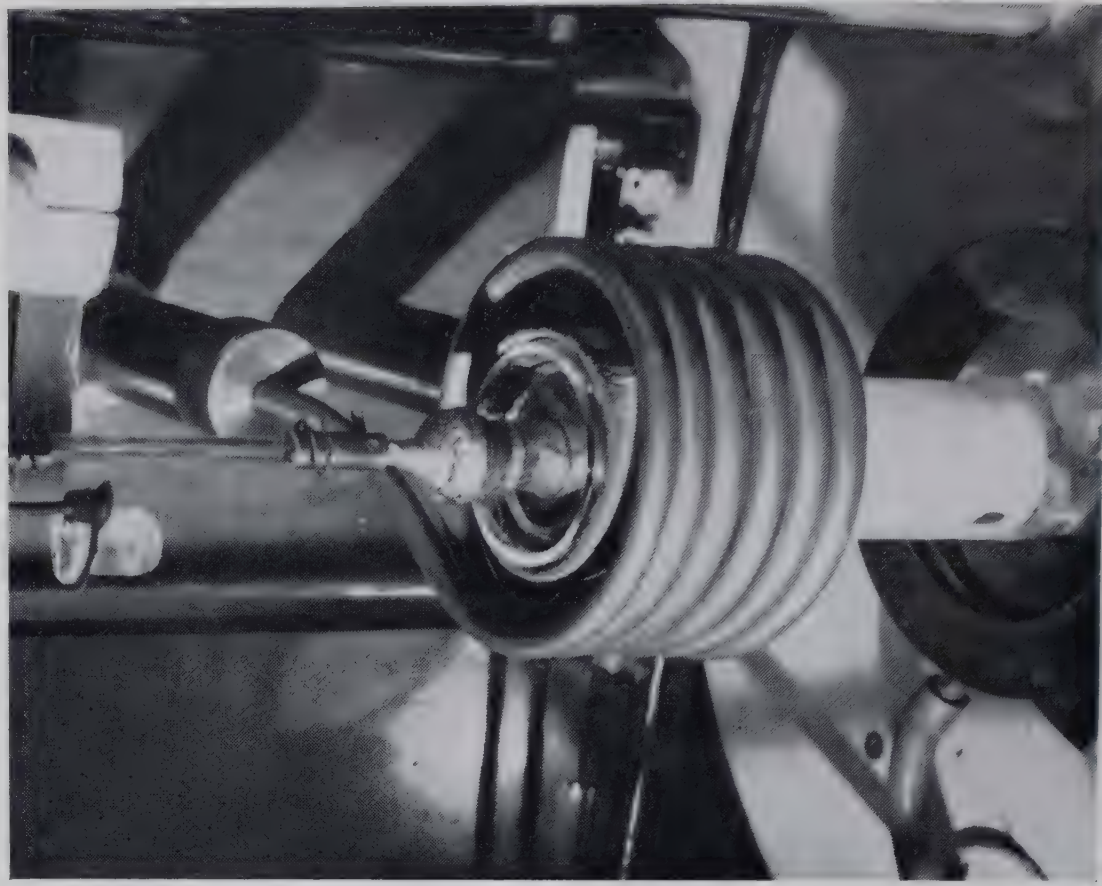


PLATE III. Apparatus shown in Plate II during withdrawal of a single crystal from a molten bath

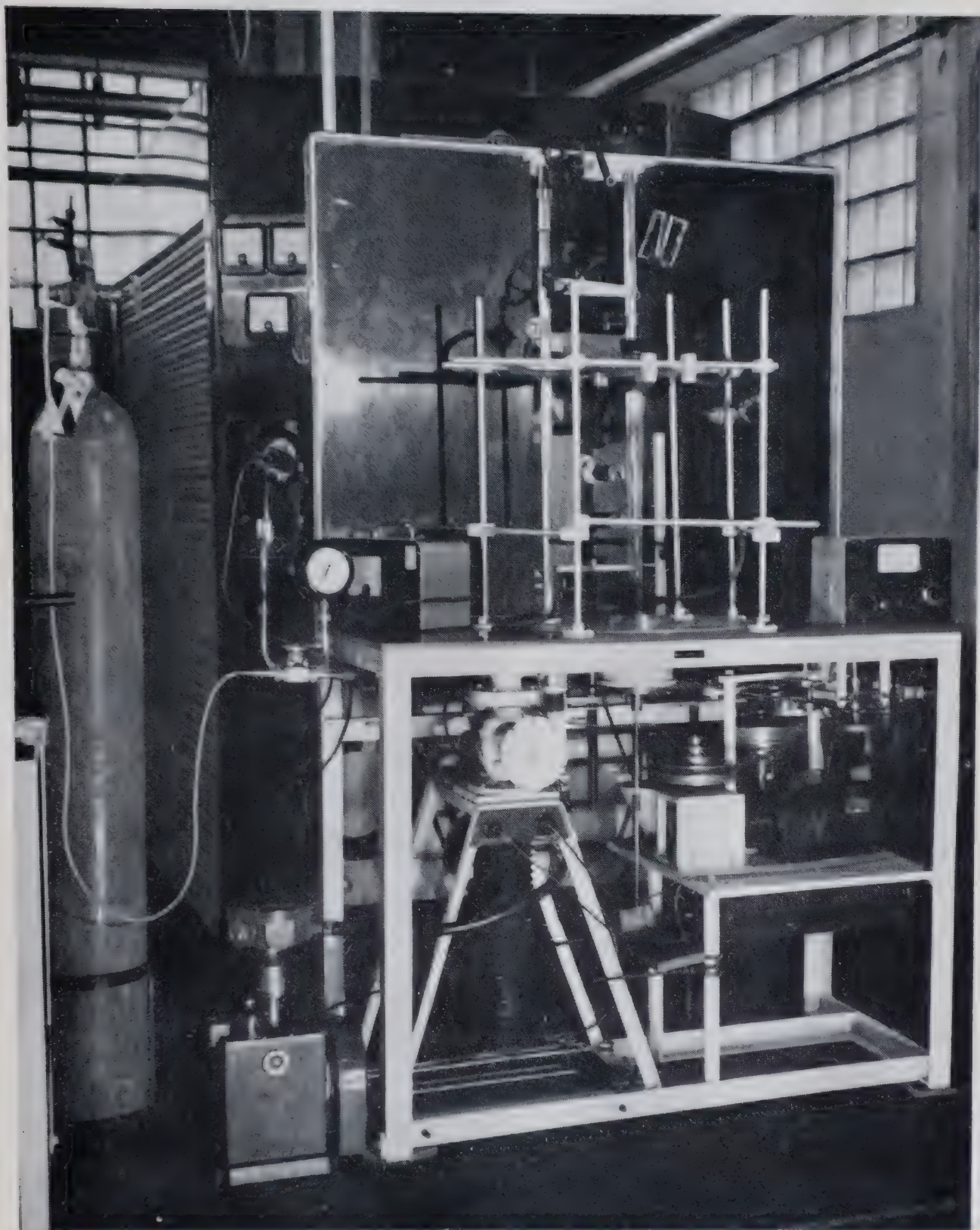


PLATE IV. Equipment for the zone refining of Silicon by the Floating Zone technique

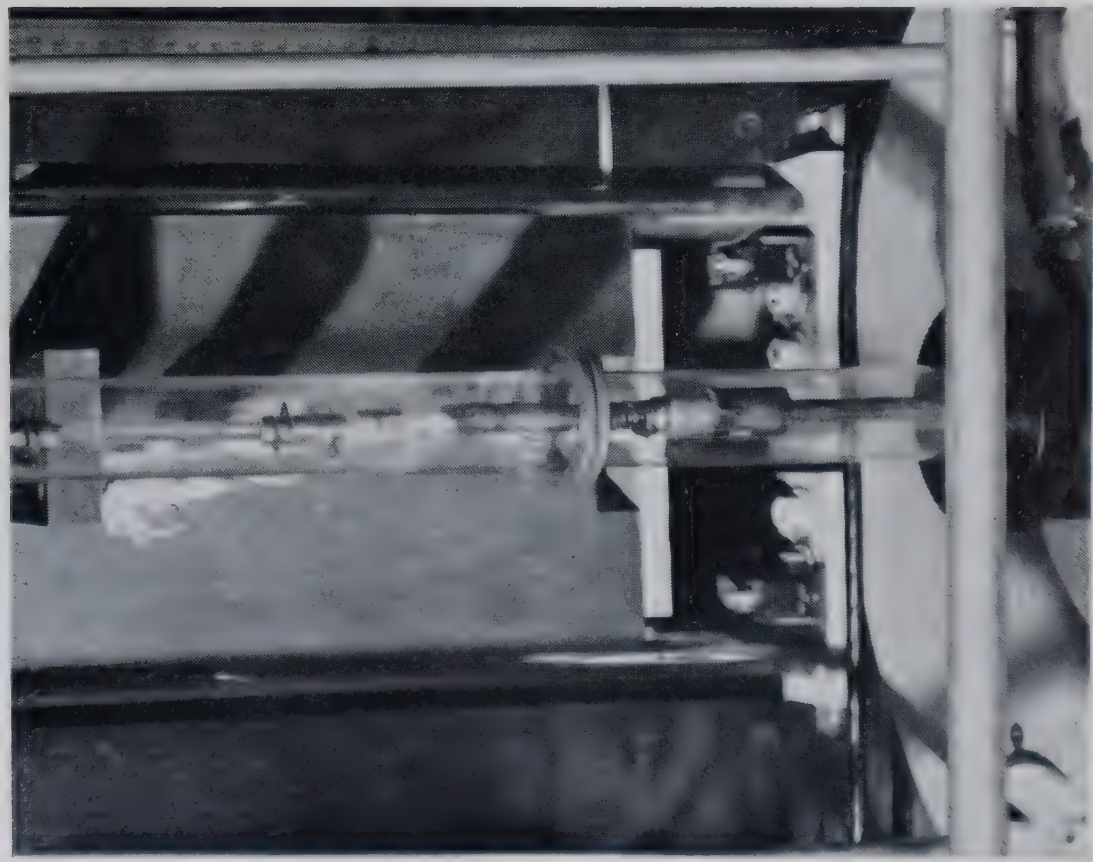


PLATE V. Detail of the Vacuum Chamber for the zone refining of Silicon by the Floating Zone technique

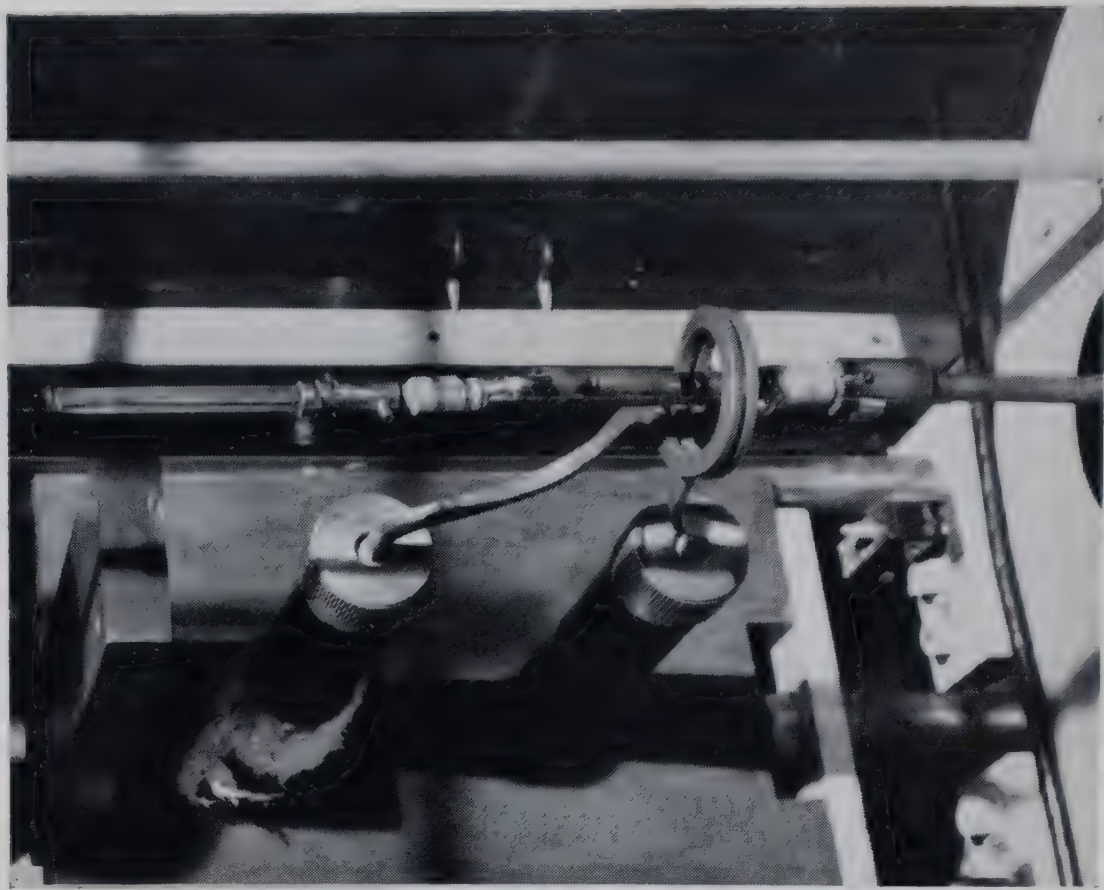


PLATE VI. Vacuum Chamber removed to show appearance of Silicon Bar during Zone Purification

ATMOSPHERE CONTROL

When dealing with materials which react with the atmosphere (sometimes well below their melting points), the zone purification process must be carried out under vacuum or in inert or reducing atmospheres. This is usually achieved by enclosing the bar and crucible in an evacuated and sealed ampoule or, alternatively, in a chamber fitted for constant evacuation or for introduction of controlled atmosphere. In either case it is often necessary to arrange for the molten zone to be generated from heat sources located outside the chamber, as shown in Fig. 12.

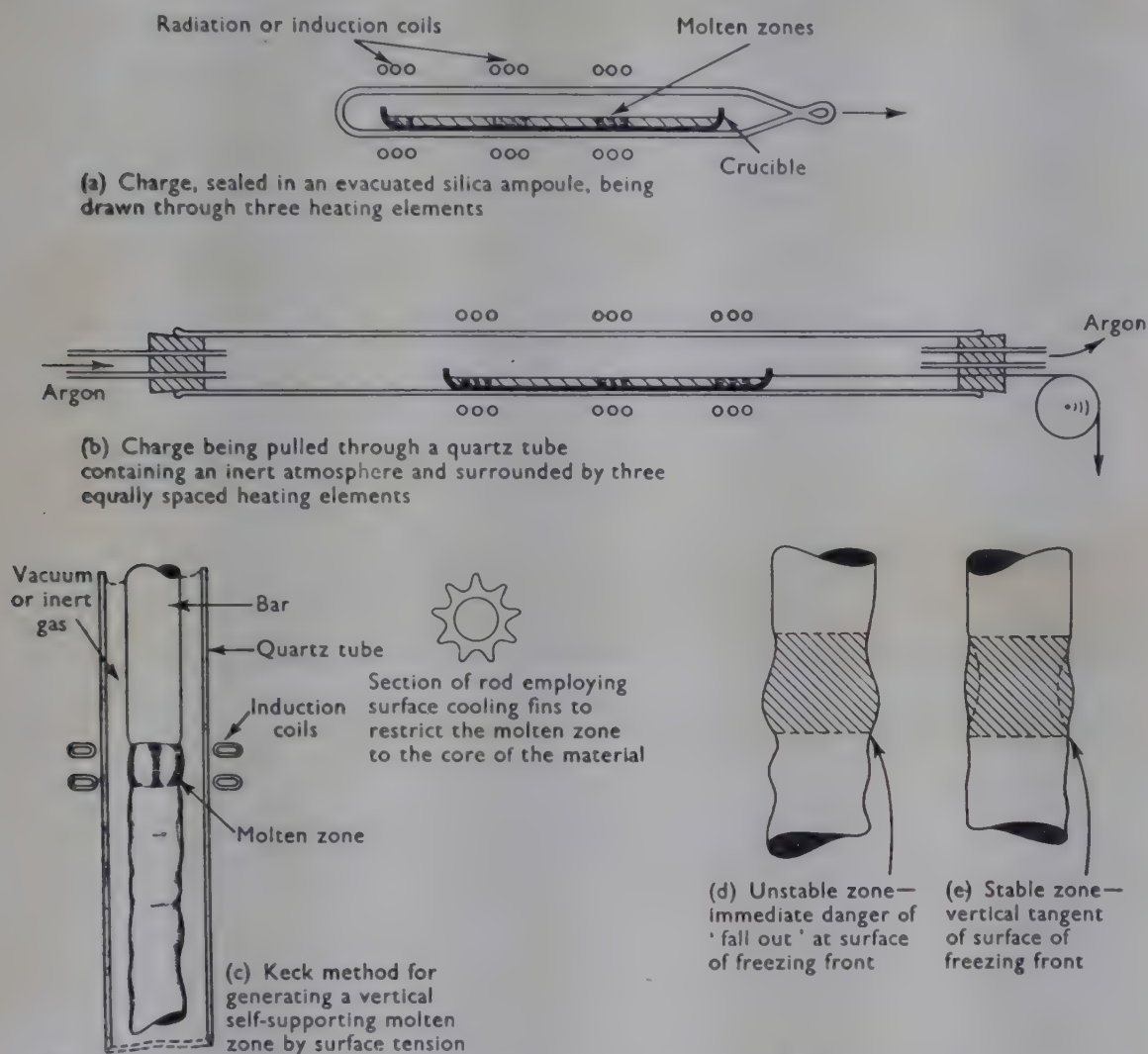


FIG. 12. Examples of horizontal and vertical methods for producing molten zones

FLOATING ZONE TECHNIQUE

The reactivity of some elements with any known crucible material, and the desire to avoid contamination at all costs, has led to the development of a special form of vertical zone refining which has been termed the 'floating zone' technique and has been described in detail by Keck.⁵ This involves the vertical support of the bar of material to be purified within, but not touching, a chamber of slightly larger diameter equipped for atmosphere control. Support of the moving molten zone is made possible in the absence of a crucible by such factors as surface tension, a thin oxide layer and the influence of an electromagnetic field. Principles of the method are shown diagrammatically in Fig. 12(c). The molten

zone is usually generated by the high frequency field from an induction coil, sometimes with the aid of a concentrator. This method will be described in detail later but it can be well imagined that particular care must be exercised in order to prevent the molten zone from collapsing. Factors influencing support of the floating zone have also been described in detail by Keck, the broad principles of which can be seen in Figs 12(d) and 12(e).

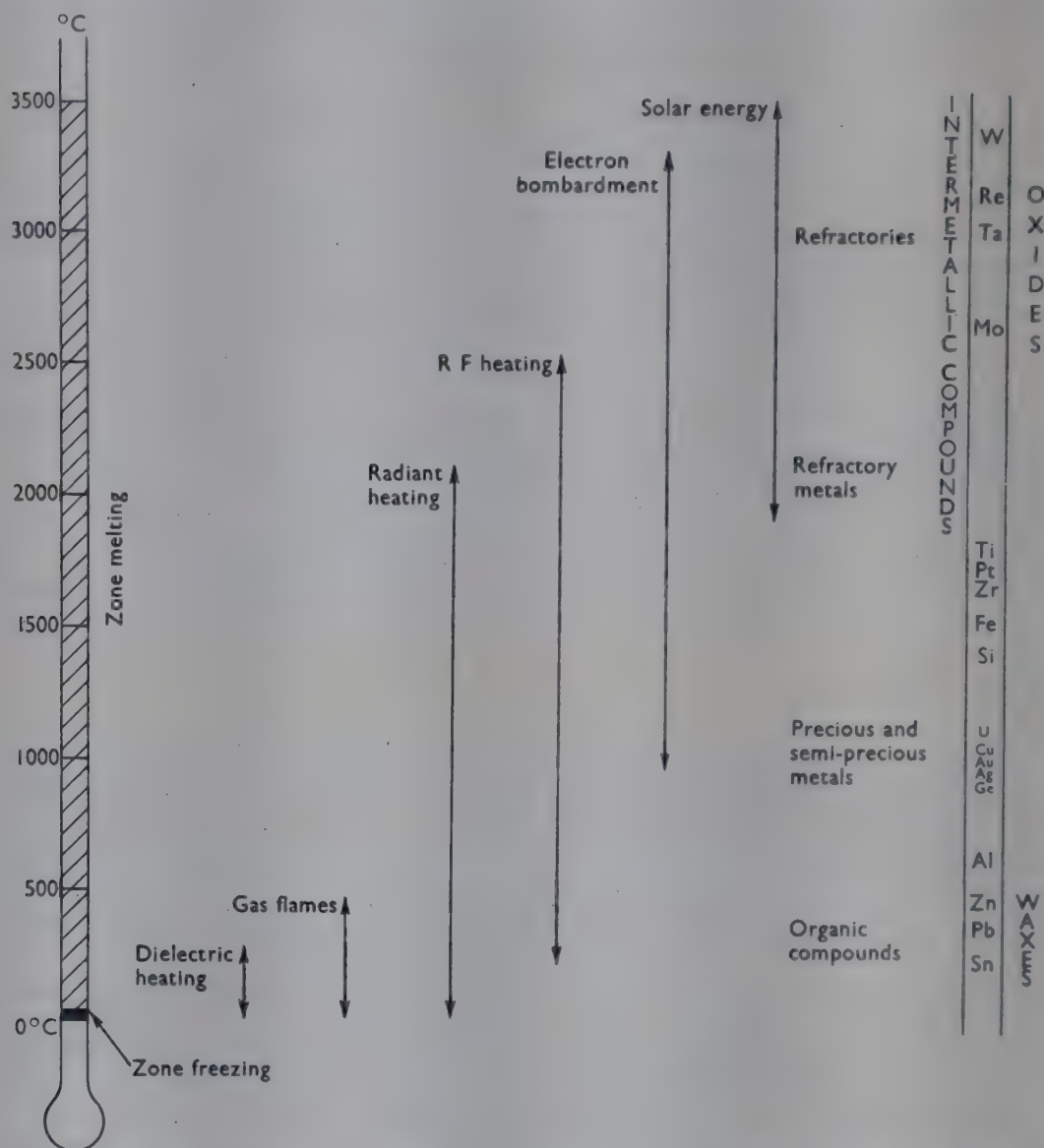


FIG. 13. Choice of heating for producing molten zones in a range of elements and compounds

Under certain conditions it is possible to aid the process by providing outer cooling fins of the same material as the bar, and by adjusting the heat balance to permit the core to be molten while the outer layers remain solid.

METHODS OF GENERATING MOLTEN ZONES

The choice of heater for generating the molten zone in the horizontal, vertical or floating zone method will depend upon the size of the bar to be purified in relation to the chemical and physical properties of the material, and the various factors already described in previous paragraphs.

Where a number of zones are to be purified simultaneously, or if vertical support is to rely solely on surface tension, it is essential that the width of the molten zone shall be as small as possible.

Molten zone width can be governed by a nice balance between :

- (i) the degree with which it is possible to focus the heat, and
- (ii) the thermal properties of the material, including radiation emissivity, latent heat, melting point and thermal conductivity.

As we have already seen, the higher the melting point and the lower the thermal conductivity, the narrower will be the molten zone. The length of the molten zone will also be influenced by the gradual accumulation of impurity which may alter the melting point and zone length. In this case the heat input must be suitably adjusted to compensate for the changes incurred as the zone is moved along the bar. Latent heat at the solidifying and melting faces will also exert its influence.

Different sources of heat and approximate ranges for their application are shown in Fig. 13.

Each method has its particular advantage in relation to the material to be purified, as will be evident from the description of several selected applications of zone refining given later.

SECONDARY EFFECTS

The preceding sections have dealt mainly with the removal of impurities from solutions having favourable segregation coefficients, and only passing mention has been made of the effect of flotation, volatilisation, sublimation and out-gassing. Some or all of these factors assume greater importance when the zone purification process is applied to a particular material.

For instance, it is possible that some impurities may sublime during zoning and recondense on cooler surfaces that have already been purified, as for example phosphorus and arsenic in silicon. This can be prevented by providing means for collecting the vaporised or evaporated elements before they have a chance to be redeposited on the parent metal. A flow of argon can be employed to sweep away gases and volatilised elements from the surface of the molten zone as they are released. The rate of release of such elements will of course be greater under vacuum, in which case strategically placed cold traps can be employed as collectors. In many cases, owing to the violence associated with liberation of gases and certain elements of higher vapour pressure, it may not be possible to proceed with zone purification until several passes have been made at temperatures slightly lower than the melting point to remove these undesirable elements; a particular case is the out-gassing of nitrogen from molybdenum. It is essential to have the quietest possible zone during the zone melting operation.

The advantages of the vertical zoning method in aiding the flotation or gravitation of inclusions and self-slagging impurities have already been mentioned.

REACTIVITY WITH CRUCIBLE MATERIALS

One of the major stumbling-blocks to the zone refining of some important materials such as titanium and zirconium arises from their reactivity with all known crucible materials, leading to gross contamination. Quite often, zone purification has to be supported by supplementary research to produce high-purity crucible materials, such as graphite, silica, alumina and beryllia.

Another source of trouble can arise from differences in the coefficients of expansion of the crucible and charge, which may lead to the fracture of the crucible after each pass, necessitating remelting in a new crucible. This points to another advantage of the unsupported floating zone technique. Other troublesome factors include high surface tension and high solid-state diffusion coefficients of the materials to be purified. From the foregoing considerations it can be readily appreciated that each material to be zone refined imposes special limitations on the design of the equipment and the procedure to be adopted.

SPECIFIC APPLICATIONS

LEAD

Perhaps the simplest form of zone purification is that being employed for purifying lead, the equipment for which is shown diagrammatically in Fig. 14.

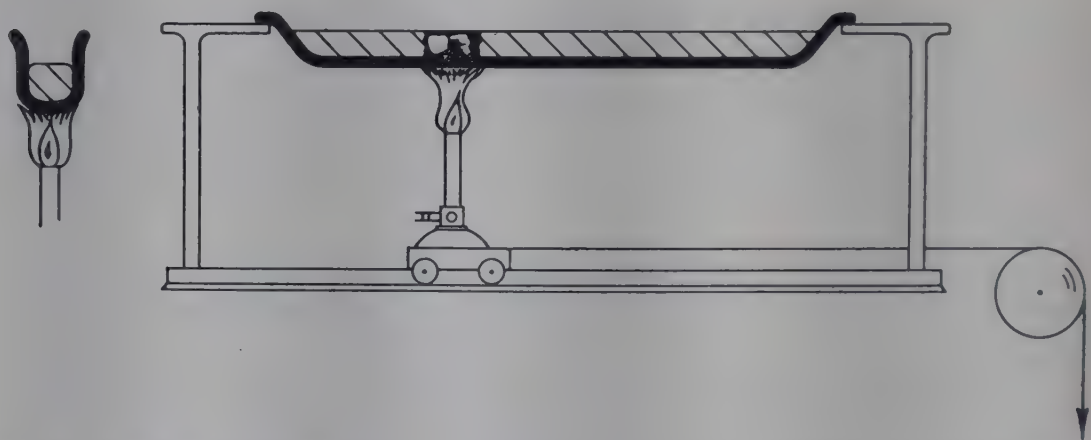


FIG. 14. Simple form of horizontal zoning in an open steel boat employed for the zone purification of lead

A boat-shaped steel mould holds the charge, which is slowly traversed over a gas flame, the ambient temperature being sufficiently steady to ensure a reasonably stable zone. Many elaborations of this apparatus have been made, in which the heater is usually an electric radiant closely surrounding a quartz tube holding the boat.

This procedure is also adopted for the purification of germanium, the equipment used being similar in principle to that already described in Fig. 12(b), where several spaced heaters are traversed simultaneously to hasten the process. Purified argon or dry hydrogen is used for the inert atmosphere around the molten metal, and the whole equipment is inclined at a low angle in order to prevent mass movement towards one end of the charge and maintain an even cross-section, as germanium contracts on melting.

Heating coils may be either electrical resistors or induction coils, the latter having the advantage of not requiring reflectors or insulators which would tend to make observation of the temperature by optical methods somewhat difficult. Another advantage of induction melting is that it promotes self-stirring within the molten zone.

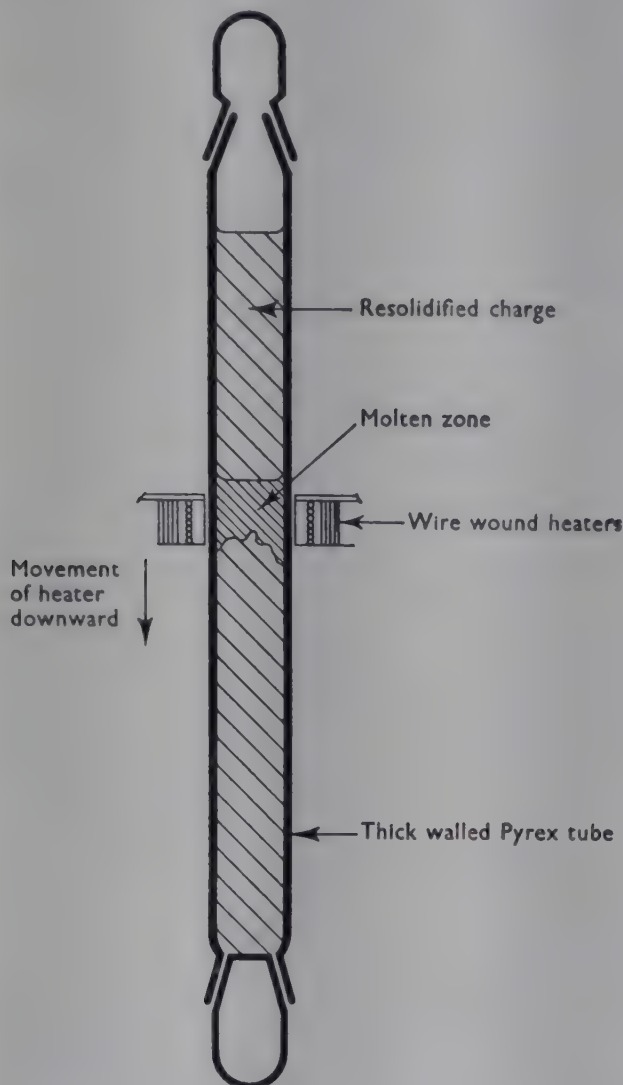


FIG. 15. Principles of the zone melting apparatus developed at the Chemical Research Laboratory, Teddington, for zone refining organic compounds

ORGANIC MATERIALS

So far, zone refining has been described mainly in relation to metals. Application of the technique to organic compounds will now be considered. The physical and thermal properties of organic compounds vary considerably from those of metals, and the design of the equipment is accordingly different. In organic compounds of low melting point and low rates of crystallisation, super-cooling may occur; the zone may be very large even with slow speeds, and, owing to surface tension and contraction, it is difficult to prevent the molten zone from seeping back into recrystallised areas.

The principles of the apparatus used by workers at the Chemical Research Laboratory, Teddington,⁶ are shown in Fig. 15.

The compound is held in a vertical glass tube and a small circular heater travels downwards. The rate of travel is largely governed by thermal considerations, which in turn are influenced by the cross-section of the bar, the difference between the melting point and the ambient temperature, and the inherent physical properties of the material. Development of the apparatus was aided by using naphthalene containing small quantities of induline as an indicator. In this apparatus, seven

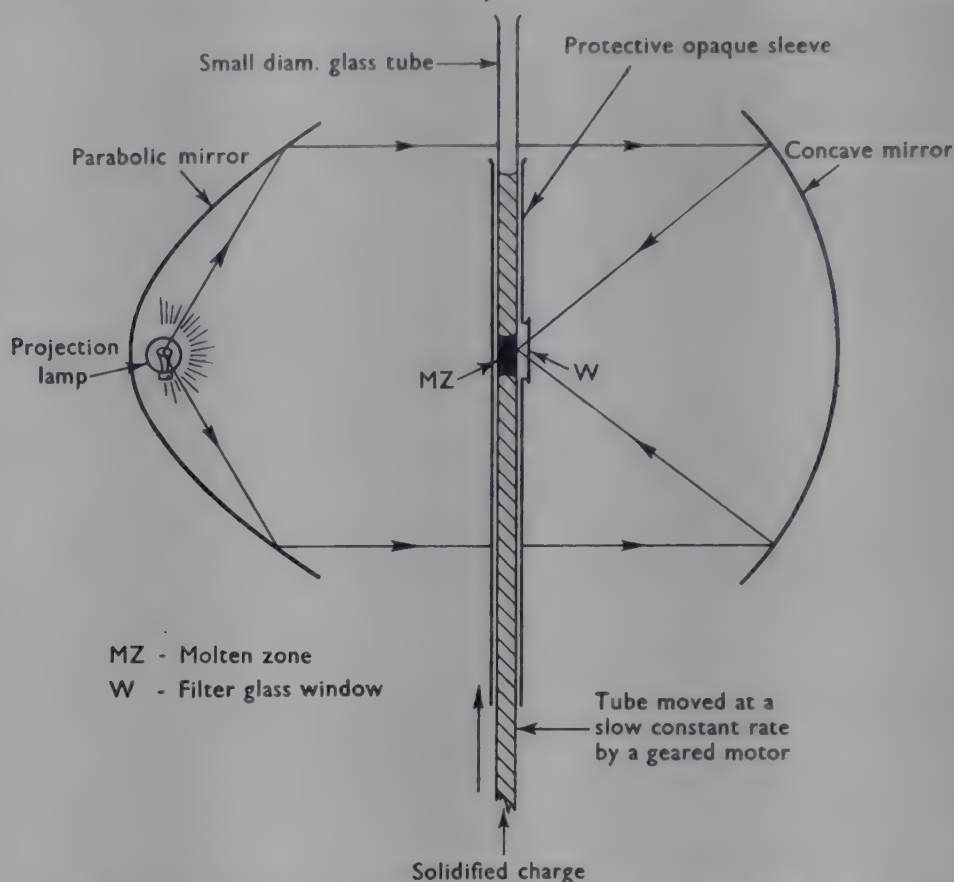


FIG. 16. Semi-micro zone melting apparatus, developed at the Chemical Research Laboratory, Teddington

passes at a rate of 1.5 in. per hour reduced the induline content to extremely small amounts, as indicated by the complete removal of the blue coloration. In a similar experiment, with 0.2 per cent of anthracene in naphthalene, the anthracene concentration was reduced to 0.00002 per cent after seven passes, as indicated by comparative fluorescence under ultraviolet light.

A novel improvement to this method, on a semi-micro scale, also attributable to workers at C.R.L.,⁷ has been to generate the small molten zone by means of heat from the filament of an incandescent lamp, focused on the bar with the aid of a reflector and a concave mirror, as illustrated in Fig. 16.

In this case the charge is very small and is contained in a glass tube of small diameter moved at a controlled rate and surrounded by a sleeve which acts as a heat and light insulator.

ATOMIC ENERGY APPLICATIONS

Reverting to metals, the technique has recently been applied in the atomic energy field, where obvious advantages are to be gained by the

use of a process that will remove undesirable impurities in new uranium fuel elements or fission products from spent fuel elements. A method used and published by the Atomic Energy Research Establishment, Harwell⁸ is shown in Fig. 17.

The uranium charge is contained in a beryllia crucible held vertically in a vacuum chamber as shown. A molten zone is generated by a molybdenum resistor surrounded by tantalum radiation shields located

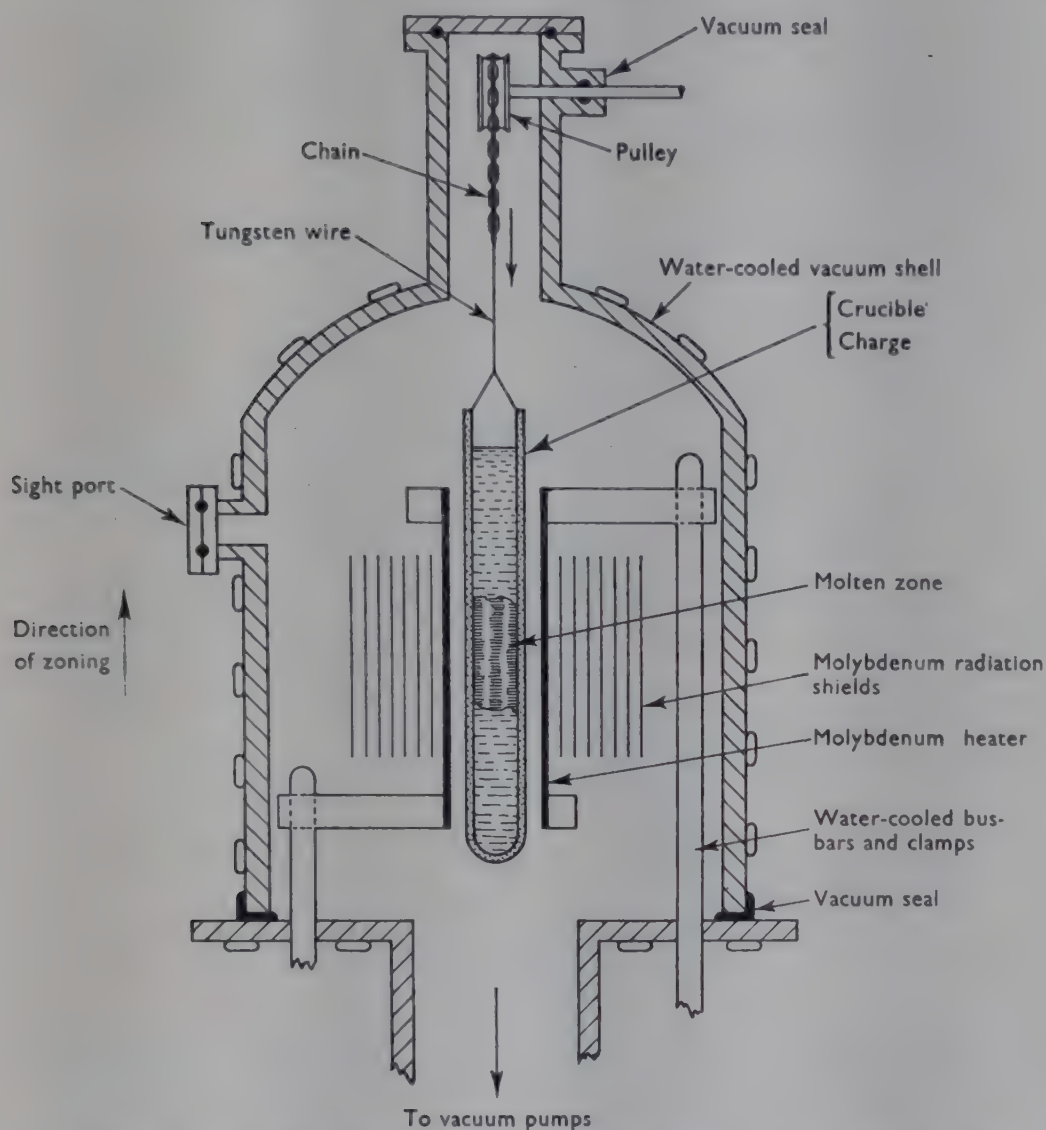


FIG. 17. Method for zone refining uranium in a vacuum chamber

inside the water-cooled vacuum chamber. The crucible is then lowered slowly through the hot area by means of a winding mechanism introduced through a Wilson seal. This causes a fairly wide molten zone to traverse the charge held in the crucible. Unfortunately, the differences in thermal contraction between the uranium and the crucible material restrict this method to a single pass per crucible, and a fresh beryllia tube must be charged with the ingot each time.

It is also possible to zone-refine a bar of uranium by the unsupported floating zone technique in similar equipment to that now being employed for silicon. This possibly represents one of the most recent fields in

which the zone-refining technique has been applied, and the apparatus developed for this purpose at the Admiralty Materials Laboratory is shown in detail in Fig. 18 and Plate IV.

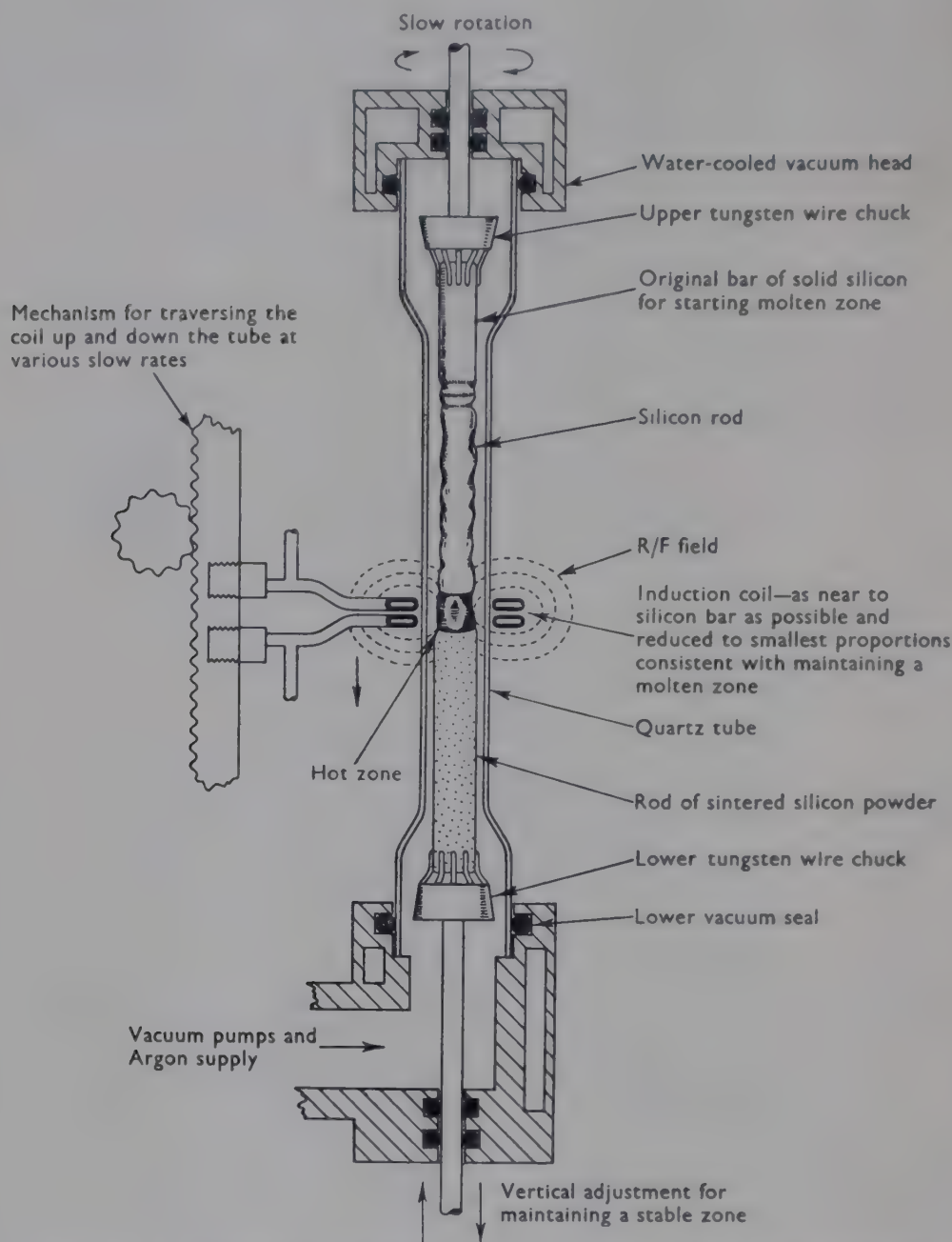


FIG. 18. Equipment for the zone refining of Silicon by the Floating Zone technique

SILICON

An unsupported floating zone is induced in a bar of silicon, which is supported from each end in a clear quartz vacuum chamber, by a small high-frequency induction coil located as close to the bar as the quartz tube will permit. In this manner it has been found possible to proceed directly to single crystal form from a bar of sintered high-purity silicon powder. Susception (*i.e.* the self-generation of heat by magnetic eddy-currents induced by the high frequency field) is difficult in silicon and almost impossible in its sintered powder form without the aid of a 'susceptor'. It can be assisted by a molybdenum or carbon ring surrounding the bar in a position beyond the area to be zoned, or by the heat of a

localised gas discharge arranged by the temporary introduction of low pressure argon into the vacuum chamber. A molten zone can also be induced by incorporating a piece of solid silicon in the sintered powder at a selected point. Once the temperature of the silicon reaches its melting point, the powder may be simultaneously melted and zoned by movement of the induction coil. It demands considerable skill and practice to maintain an even cross-section during zoning. This may be aided by constant rotation of the upper section and the adjustment of zone diameter by vertical manipulation of the ends through suitable vacuum seals.

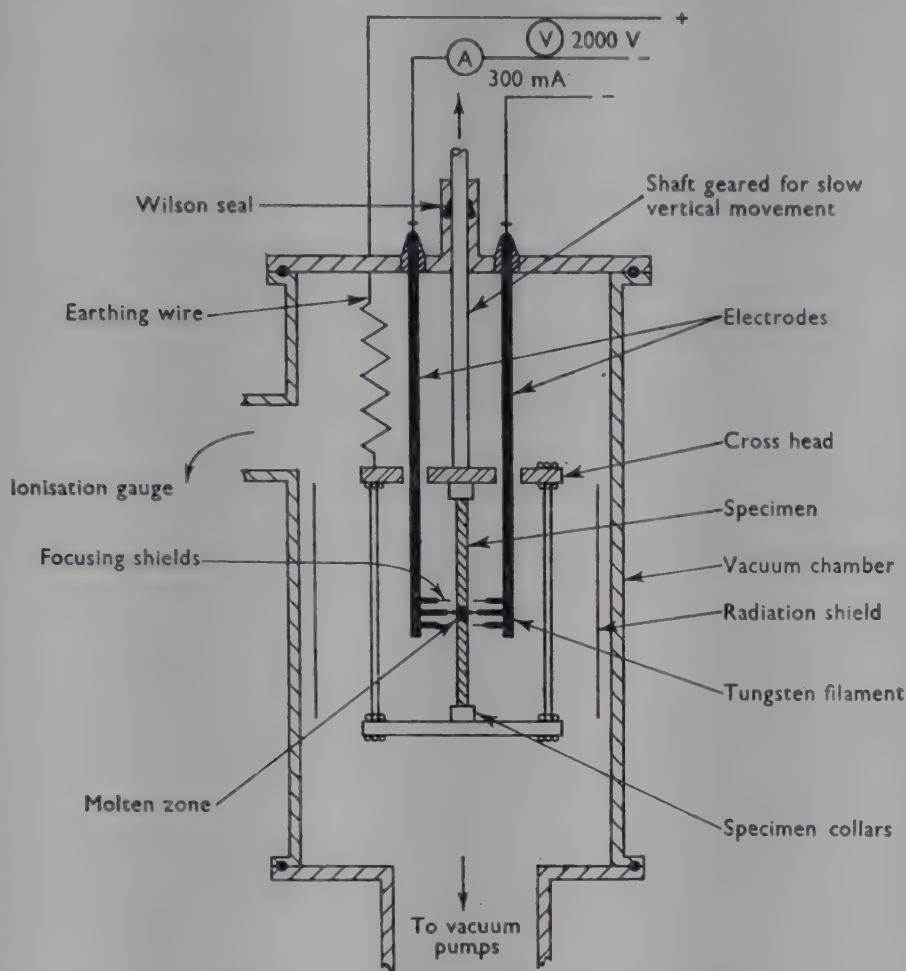


FIG. 19. Zone purification by electron bombardment. (The only limiting factors are a low enough vacuum and sufficient surface conduction to start the flow of electrons)

The appearance of a sintered bar during zone refining can be seen in Plates V and VI. The process is aided by delicate control of energy input, which necessitates constant observation through the quartz tube. If a single crystal is required, a crystal seed must be incorporated at one end of the sintered bar.

An alternative to a high-frequency field, exhibited at the 1956 Physical Society Exhibition by the Services Electronics Research Laboratory,⁹ produces a hot zone by focusing a stream of electrons accelerated by a few kilovolts and emitted from a heated tungsten loop surrounding the bar inside a vacuum chamber. The molten zone can be controlled to a narrow band by focusing shields placed above and below the tungsten loop, as shown in Fig. 19.

So far, this technique has been limited to bars of fairly small diameter, but a large number of the rarer metals in single and polycrystalline form have been zone-refined in this type of equipment.

Power requirements for a $\frac{1}{2}$ cm diameter bar of tungsten or rhenium are about a kilowatt at a few tenths of an ampere and several kilovolts. Provided the material to be zone-purified has sufficient inherent or artificially produced surface conductance, there is scarcely any limit to the range of materials to which this method can be applied.

GENERAL FIELDS OF APPLICATION

Fields of application for the zone-refining technique are increasing steadily as the demand grows for elements of higher purity so as to study their intrinsic properties. Its application has not yet, however, reached the commercial scale, and the method is still very much the tool of the research worker. Zone refining is still a relatively expensive and low-yield process, but even so it has many economical justifications where the materials required are practically unobtainable by other means. Its chief application hitherto has undoubtedly been in the semi-conductor field, where it can now be considered to have reached a limited commercial scale. Its use for the preparation of standards for spectrographic analysis and other purposes is being extended, while application for the production of very pure metals for intimate study of their chemical, physical and mechanical properties is stimulating many fields of solid-state research.

METALS

Studies of deformation processes responsible for yielding, creep and sudden catastrophic fracture under static or cyclic loading are often confused by the presence of impurities which take up strategic positions on the metal lattice or crystal planes. The production of many metals in an extremely high state of purity is now being achieved and is providing physicists and metallurgists with evidence from practical experiment to support dislocation theories. For instance, the brittleness of some metals, once thought to be an inherent property, has now been shown to arise from the presence of trace impurities. Metals which have been successfully purified by zone refining include iron, aluminium, copper, tungsten, rhenium, titanium, zirconium, lead, uranium, tin, bismuth, antimony and gallium. The technique has also been used for the production of high-purity platinum for standard thermocouples and homogeneous alloys for standard electrical resistance wire.

Some idea of the degree of purity achieved by various workers with the zone refining technique is given in Table I.

TRANSISTOR MATERIALS

The rapid development of transistors has brought about the need for certain elements to be produced in a high state of purity, particularly germanium, silicon and gallium. It is therefore in this field that the zone purification process has begun to approach a commercial scale and where the purified elements have received the greatest attention by

TABLE I
DEGREES OF PURITY ACHIEVED BY VARIOUS WORKERS BY ZONE REFINING

Substance		Impurities (p.p.m.)										Reference
		Sb	Cr	Co	Fe	Mn	Ni	Si	Ag	Sn		
Cu	Before	10 ³	10 ³	10 ³	10 ³	10 ³	10 ³	10 ³	10 ³	10 ³	10	
	After	No	1	60	10	No	10	No	No	No		
Sb	Before	Ni	Pb	As	Ag	Cu	Fe	Si	Sn		11	
	After	1-30 × 10 ³ <50	1-30 × 10 ³ <3 × 10 ³	1-30 × 10 ³ 1-30 × 10 ³	<3 × 10 ³ <50	<3 × 10 ³ <3 × 10 ³	<50 <3 × 10 ³	<50 <10	<50 <10			
Sn	Before	Pb	Cu	Fe							11	
	After	10 1	0.3 0.1	5 4								
Fe	Before	C	Cu	Ni	N							
	After	2.5 × 10 ³ 800	6 × 10 ³ 1.5 × 10 ³	6 × 10 ³ 6 × 10 ³	1.4 × 10 ³ 400							
Re	Before	Ca	Mg	Na	K	Si						
	After	500 10 ³	10 ³ 50	10 ³ No	10 ⁴ No	2 × 10 ⁴ 500						
U	Before	C	O	N	Ce	Zr	Sr	Ru	(reduction)		8	
	After	810 270	110 30	80 8	45%	75%	90%	10%				
Al (99.99%)	Before	Cu	Fe	Si							12	
	After	10-11 0.4-0.6	26-29 6	30-37 3								
Naphthalene	Before	Anthracene									6	
	After	2 × 10 ³ 0.2										
Ga	Before	Cu	Fe	Ca	Mn	Si	Al	Ag			2	
	After	10-70 <1	10-70 <1	10-70 <1	10-70 <1	10-70 <1	10-70 <1	10-70 <1				
Ge	After	Cu	Ni	Fe	(by electrical measurement)						2	
	After	<10 ⁻⁴	<10 ⁻⁴	<10 ⁻⁴	(by mass spectrograph)							
Si	After	O	B	Fe	As	Sb	Cu	Zn	P		Various Workers	
		1	4 × 10 ¹³ (atoms per cc)	0.1	10 ⁻⁴	2 × 10 ⁻³	10 ⁻³	7 × 10 ⁻³	3 × 10 ¹¹ (atoms per cc)			

analytical chemists. Purification, particularly of germanium, has reached the stage where the impurity content is not detectable by normal analytical methods and the order of conductivity-producing elements present is estimated by resistivity measurements. Concentrations of impurity elements as low as 10^{-7} parts per million for most elements, except dissolved oxygen and hydrogen, are now achieved in zone-purified germanium.

In the case of silicon, although a considerable number of undesirable impurity elements have segregation coefficients favourable to removal by zone refining, one of its most prominent impurities, boron, has a k value of 0.8 and therefore cannot be removed by straight zone refining. Recently, however, it has been found that if zoning is carried out in a stream of wet hydrogen it is possible to liberate the boron as oxide from the surface of the molten zone and to collect it on water-cooled surfaces before it can be re-deposited on the cooler surfaces of the bar.

Compounds such as gallium arsenide and indium antimonide are being zone-refined. With some compounds whose parent element is unsuited to zone purification as a result of its high vapour pressure, zone refining has to be carried out on one of its more favourable compounds, which may then be reconverted to the element.

The field of semi-conductors makes the greatest use of variations in the zone-refining process to produce compositional gradients, deliberate reinoculation with acceptor or donor elements and the production of the final material in single or modified crystal form, although single crystals of the purified material are often more conveniently produced by the Kyropoulos technique.

ORGANIC COMPOUNDS

While inorganic compounds are usually more easily purified by crystallisation from solution, zone purification offers an attractive method for some organic compounds whose vapour pressure and ease of decomposition are unfavourable to fractional distillation. The production of super-pure compositions as physical and chemical standards is a continual requirement, and organic compounds such as benzoic acid, pyrene, anthracene, morphine and chrysene have already been successfully purified in this manner. Examples of applications to inorganic compounds include the purification of ceramics, where solar energy is being utilised to obtain the high temperatures necessary for the generation of a molten zone in refractory oxides and intermetallic compounds.

REMOVAL OF FISSION PRODUCTS

The removal of poisons and long-life fission products from spent fuel elements from nuclear reactors offers attractive future possibilities for this technique. Such impurities are removed either by flotation or segregation, or by a self-slugging process during zoning. The possibility of developing the unsupported floating zone technique as a continuous process could be an important contribution to the future economy of atomic energy. The separation of isotopes, however, is not a promising field, owing to the operative segregation coefficients normally being close to unity, but some success may be expected with heavy water.

CONCLUSIONS

The process of zone refining has now taken its place as one of the standard methods available for the purification of materials. Its application is simple in concept, but where this is appropriate the degree of success achieved will reflect the amount of attention given to each aspect of the process. Experiments on the zone refining of copper by Tolmie and Robins¹⁰ have indicated a good correlation between segregation coefficients determined from phase equilibrium diagrams and those obtained experimentally. Knowledge of phase equilibria, therefore, provides a first indication of the chances of success.

Perhaps the most important attribute of the process is the amazing degree of purity that can be obtained in materials difficult to purify thoroughly by other means. This is of particular importance today in the preparation of semi-conductor materials, some aspects of which have been mentioned here.

The analytical determination of the extremely small quantities of impurity elements is not easy, and the production of transistor materials with the desired degree of purity has presented a new challenge to the analytical chemist. The nature of this challenge may be appreciated when it is remembered that impurities of concentrations of 10^{-9} and less are significant in such materials. The development of radioactivation analysis is the most important advance here, and for the appropriate impurity elements the necessary order of sensitivity is usually obtained. The classic example is provided by the determination of arsenic in germanium,¹³ the method being sensitive to one part in 10^8 . Recent work at the Admiralty Materials Laboratory has indicated the following sensitivities for the determination of certain elements in silicon by radioactivation: arsenic 10^{-8} ; antimony 10^{-9} ; copper 4×10^{-9} ; gold 10^{-10} ; phosphorus 2×10^{-8} ; potassium 4×10^{-9} ; sodium 10^{-9} . Unfortunately, the radioactivation method is applicable only where the impurity element on neutron irradiation generates suitable radioactive isotopes sufficiently long-lived to permit a few hours of chemical manipulation before measurement.

For other elements, such as boron and aluminium, for which radioactivation is useless, alternative methods are having to be developed. For example, methods based on optical emission spectrometry, mass spectrometry and square-wave polarography are being investigated by various workers. It is not considered feasible to attempt to improve the sensitivity of absorptiometric methods for these elements, as there seems no likelihood of such methods ever reaching the sensitivity desired, though they are excellent for the assessment of purity prior to zone refining. There appears to be plenty of scope even yet for improving the sensitivity of spectrographic methods for such elements, and current work is expected to produce improvements of at least one order of magnitude. Another very promising approach is the use of the comparatively new technique of spectrofluorimetry, and much work in this field is being undertaken at the Admiralty Materials Laboratory, where a method for estimating boron in silicon having an intrinsic sensitivity of at least one part in 10^8 is being investigated.

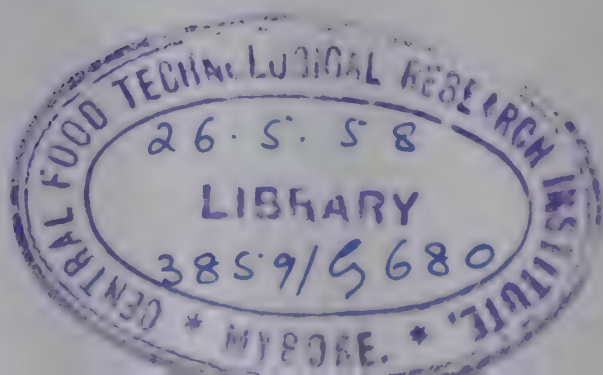
In developing such methods the analytical chemist is now frequently faced with the difficulty that the reagents he needs to use for the analysis are less pure than the substance he is analysing. Here again is an opportunity to apply the technique of zone refining at some stage in the production of sufficiently pure chemical reagents, and perhaps we may soon see marketed a new group of hyper-pure analytical reagents (at an appropriate cost), taking its place beside the now indispensable analytical and microanalytical reagents of well-known manufacture.

The compilation of this review owes much to a number of research workers at various centres, and reference should be made to their published works, some of which have already been quoted, for a more detailed account of the various factors involved. If this monograph does no more than introduce the subject to those who are likely to find the zone-refining process useful in their respective fields of endeavour and refer them to the authorities on the subject, then it will have succeeded in its object.

Grateful acknowledgment is made to Mr E. J. Vaughan for his advice and encouragement in the production of this review, and to my colleagues at the Admiralty Materials Laboratory for their help in its compilation. The paper is produced by permission of the Admiralty.

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